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Journal of the

American Leather Chemists Association

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George W. Priest, to Eclipse Tanning Co., Newark, N. J.

Elting C. Stillwell, to c/o of Davis and Geck, 27 S. Oxford Street, Brooklyn, N. Y.

NINTH ANNUAL MEETING.

The Ninth Annual Meeting of the American Leather Chemists' Association was held at Washington, D. C., December 5th, 6th and 7th, 1912, at the Hotel Raleigh. President F. P. Veitch presided. H. C. Reed, Secretary. Among those present at the meeting were:

Thomas Blackadder, Damascus, Va.; Lloyd Balderston, Ridgway, Pa.; H. H. Hurt, Covington, Va.; Charles M. Kernohan, Newark, N. J.; Walter H. Stifel, Pittsburgh, Pa.; Thomas J. Mosser, Williamsport, Pa.; Paul M. Giesy, Washington, D. C.; R. W. Griffith, New York; Charles R. Oberfell, Harrisonburg, Va.; Frank M. Loveland, Du Bois, Pa.; W. K. Alsop, Ridgway, Pa.; T. A. Faust, Newark, N. J.; Charles C. Smoot, III., North Wilkesboro, N. C.; J. S. Rogers, Washington, D. C.; C. A. Backer, Boston, Mass.; F. H. Small, Worcester, Mass.; J. V. R. Evans, Sheboygan, Wis.; F. P. Veitch, Washington, D. C.; R. H. Wisdom, Stamford, Conn.; K. Ruppenthal, New York; E. J. White, Philadelphia, Pa.; W. H. Teas, Marion, Va.; W. G. Sprinkel, North Wilkesboro, N. C.; W. H. Dickerson, Muskegon, Wis.; W. F. Wilson, Lynchburg, Va.; W. A. Fox, Kenosha, Wis.; Reinhold Lang, Berlin, Ontario; W. W. Stockberger, Washington, D. C.; H. C. Reed, Stamford, Conn.; Charles R. Delaney, Hanover, Pa.; Allen Rogers, Brooklyn, N. Y.; Philip S. Tilden, Philadelphia, Pa.; E. J. Haley, New York; John H. Yocum, Newark, N. J.; Sigmund Saxe, New York; Dwight W. Vaughan, Salem, Mass.; C. W. Norris, New York; H. L. Clough, Boston, Mass.; William Klaber, Camden, N. J.; Oma Carr, Canton, N. C.: G. A. Kerr, Lynchburg, Va.; F. A. Loveland, Corry, Pa.; J. A. Connelly, Ludlow, Pa.; N. P. Cutler, Ludlow, Pa.; G. H. Tousey, Muskegon, Wis.; Cudworth Beye, Chicago, Ill.; V. A. Wallin, Grand Rapids, Mich.; John E. Wilder, Chicago, Ill.; J. C. Cover, New York; C. B. Bacon, Washington, D. C.

Thursday, December 5, 10.30 *A. M.*

MR. VEITCH: The Association will be in order.

This is the ninth meeting of this Association, which has continued to grow in membership and in attendance at the annual meeting. The growth of the Association is positive evidence

that the tanning industry is finding the science of chemistry of considerable, if not essential, help in the industry. This Association is to be congratulated that this is true, and the tanning industry itself is to be congratulated that they have so promptly made use of the knowledge and service of chemistry in their field.

While the work of the Association has been very successful and important, I think it is true that we are only at the beginning of our opportunities. The devising and improving of the methods of analysis is in fact a minor matter. The problem of the making of better leathers at less cost is primarily the purpose of the use of chemistry in the tanning industry, and I want to urge upon the industry the advisability of letting the chemist work up as rapidly as he possibly can to the position of the tanner or superintendent of the tannery, where he should be of more service to the industry than any one who is not thus equipped.

The chemist has been for years one of the chief promotive factors of the country, and here, as in other walks of life, he can still exert his influence, and I want to again bespeak the advisability and necessity of making the best leather that possibly can be made. We all know that the imports of the raw materials are very large. I think it behooves us to reduce these as much as possible by making the maximum use of our native raw supplies, making as good a product as possibly can be made.

The Secretary's report for 1912 was then read by H. C. Reed, as follows:

Total Active Members, Dec., 1, 1912					121
Total Associate Members, Dec., 1, 1912					139
Total Membership, Dec., 1, 1912					260
Active Members elected during the year		18			
Associate Members elected during the year		21			
Total additions			39		
Active Members resigned during the year		5			
Active Members died during the year		1			
Associate Members resigned during the year		6			
Associate Members died during the year		3			
Total losses			15		
Net gain				24	
Total Membership, Dec. 1, 1911	236				
Net gain during 1912	24				
Total Membership, Dec. 1, 1912	260				

DEATHS DURING 1912.

Active.

Dr. August M. Kilp, 241 West 126th St., New York City.

Associate.

John O. Pierson, c/o Taber Pump Co., Buffalo, New York.
Patrick Reilly, Mott and Passaic Sts., Newark, New Jersey.
Henry Vom Berge, Perry and Mississippi Sts., Buffalo, New York.

H. C. REED, Sec'y.

The Treasurer's report showed a balance of $793. T. A. Faust and C. C. Smoot, III., were appointed to audit the accounts of the Treasurer.

The report of the Committee on Disposal of Tannery Waste was then read by F. P. Veitch, Chairman. (This paper will be found elsewhere in this number of the JOURNAL.) Some discussion followed.

Charles R. Oberfell then read the report of the Committee on Oils and Fats (published in the December JOURNAL). A summary of the discussion which followed appears in this number.

R. W. Griffith then read a paper by Douglas McCandlish and John Arthur Wilson on the Determination of Alkaline Sulphides (published in this issue).

The afternoon session, Thursday, December 5, was called to order by Vice-President Griffith. Mr. C. C. Smoot, III., read a paper, "How Long Should Chestnut Oak Bark Be Stored Before Leaching." (This paper will appear in the February JOURNAL.) After some discussion on Mr. Smoot's paper, Dr. W. W. Stockberger was called on for his paper on The Geographical Distribution of Tannin Plants (printed in this number).

Charles R. Delaney then read a paper on Comparative Extract Analysis, which called out a rather long discussion. (This will appear in the February JOURNAL.)

The Auditing Committee reported that the Treasurer's account had been examined and found correct.

The chair then called on J. H. Yocum for a report from the Committee on Salt Stains. Mr. Yocum replied that no committee work had been done, but he read a paper on the subject, which appears elsewhere in this number. Discussion followed

the reading of Mr. Yocum's paper, and at about 5.15 the Association adjourned.

At the third session, Friday morning, December 6th, President Veitch in the chair, the first business was the report of the Committee on Comparative Analysis, W. K. Alsop, Chairman (published in the December, 1912, JOURNAL). The reading of this report was followed by a long discussion, a summary of which will be published later.

F. H. Small, Chairman, then read the report of the Committee on Analysis of Sulphite-cellulose Liquors, which also called out much discussion. Several members complimented the committee on the thorough and comprehensive study of the problem shown in the report. (This report and a summary of the discussion will appear in the JOURNAL later.)

At the session on Friday afternoon Vice-President Griffith presided.

The report of the Committee on Acidity of Tan Liquors, L. Balderston, Chairman (published in the December, 1912, JOURNAL), was read.

L. Balderston read a paper on the Electrometric Measurement of Acidity, the apparatus of Wood, Sand and Law being shown on the table. (This paper will be printed in a future issue of the JOURNAL.)

Professor H. R. Procter had sent to President Veitch a paper entitled "Note on the Pickling Process," which was now read. It will be found elsewhere in this issue.

Frank M. Loveland read a paper, "Notes on Discussion," which called out some discussion, chiefly in regard to blends of sulphite-cellulose extract. (This paper will be published later.)

The Secretary now read a letter from Alfred Seymour-Jones, Chairman of the International Commission on the Preservation, Cure and Disinfection of Hides and Skins, outlining the work of the Commission and calling special attention to the formic-mercury process of disinfection. (See JOURNAL, Vol. VI, p. 85.) Some discussion followed. (The letter and discussion will appear in the JOURNAL later.)

F. M. Loveland now read the report of the Committee on Detection and Estimation of Tanning Materials in Admixture, A.

W. Hoppenstedt, Chairman (published in the December, 1912, JOURNAL). H. C. Reed remarked that he had tried the alcutin test (see JOURNAL, Vol. VII., p. 565, October, 1912) and obtained good results.

E. J. Haley read a paper on "Myrobalan Arbitration," which was followed by a long discussion. Adjournment at about 5.20.

In the evening a banquet was held at the Café Republique, which visitors were invited to attend as the guests of the Association.

The fifth session convened on Saturday morning with President Veitch in the chair. H. C. Reed, Chairman, presented a report from the Committee on Color Testing of Tanning Materials, showing color tests made on several kinds of skin. (Report and discussion will appear in the JOURNAL later.)

C. F. Sammet then spoke on "The Identification of Tanned Skins." He showed wax impressions of the grain of several kinds of leather, and photomicrographs made from them.

The report of the Committee on Leather Analysis was presented by the Chairman, F. P. Veitch. (This report was published in the JOURNAL, December, 1912.) Dr. Pæssler, of the Freiberg Research Institute, participated in the work of the Leather Analysis Committee. His report was not received in time to be included in the published report, but was now presented by Mr. Veitch, and will appear in the JOURNAL later.

As Tellers for the election of officers, F. M. Loveland and C. C. Smoot, III., were appointed. W. K. Alsop was elected President; C. W. Norris, Vice-President; H. C. Reed, Secretary-Treasurer, and A. W. Hoppenstedt, member of Council. For the remaining member of Council there was no choice owing to a tie vote. The meeting was then adjourned.

The new Council met immediately after adjournment of the Convention. Messrs. Alsop, Norris, Reed, Small and Oberfell being present.

Two active and three associate members were elected.

The Editor was directed to send the JOURNAL gratuitously to the Royal Italian School of Tanning, at Turin.

A letter from the Secretary of the National Association of Tanners was read, calling attention to the vacancy caused by the

resignation of J. H. Russell from the Advisory Board. The President of the Association, W. K. Alsop, was nominated to fill the vacancy.

NOTE ON THE PICKLING PROCESS.[1]

By Henry R. Procter.

In a paper on "The Action of Dilute Acids and Salt-Solutions Upon Gelatine,"[2] published last year, the action of neutral salts in contracting the swelling produced by acids on gelatine is attributed to the osmotic pressure of the acid-ion (anion) common to both salt and acid, and it would seem to follow from this that only the salt of the *same* acid which produced the swelling could be effective. It is, however, well known that common salt (Na Cl) reduces the swelling caused by *any* acid, and the same is true in varying degrees of any pair of salt and acid. It is indeed stated in the paper quoted that "with weak acids and their salts, the effect is less marked, but quite obvious. If, however, a weak acid is used with large excess of a salt of a strong acid, the gelatine behaves as if the strong acid only were present; while the gelatine swollen with a strong acid, and treated with the salt of a weak one, naturally behaves as if the weak acid had been used." This is true, not merely of gelatine, but of animal skin; and the explanation (given in a latter part of the same paper) is "that any such combination simply leads to a quadruple equilibrium in which each acid is balanced against its own neutral salt. Thus in the case of acetic acid and sodium chloride, we have in the solution gel-ions, acet-ions, and an enormous excess of sodium and chlorine ions, and, if we imagine combination, we must, by the law of mass-action, have much gelatine chloride balanced against sodium chloride, and little gelatine acetate, balanced against sodium acetate." That this is the correct explanation will be obvious to any modern chemist; though it involves the idea, apparently repugnant to "common sense," that the strong acid, hydrochloric, is expelled from its combination with

[1] Read at the Ninth Annual Meeting of the *A. L. C. A.*, Washington, D. C., December 6, 1912.

[2] Kolloidchemische Beihefte, Bd. 11, Hefte 6-7; *Jour. Amer. Lea. Chemists' Assoc.*, June, 1911.

the strong base sodium by the joint action of the weak acetic acid, and the very weak base gelatine.

It has, however, been shown by the author experimentally, that even in the absence of gelatine, a solution of acetic acid too weak to redden methyl-orange, is rendered capable of doing so by the addition of sodium chloride, thus indicating a slight liberation of the stronger hydrochloric acid from its sodium salt by the weaker acetic acid, but in this case the decomposition is limited to the merest trace.

It seemed therefore worth while, clear as the conclusion is on theoretical grounds, to test the fact by actual analysis, as it is of both scientific and technical importance. For this purpose, 1 grm. of very carefully purified gelatine was treated with N/10 solution of pure formic acid, which was proved free from HCl. When the swelling was complete, sodium chloride was added to saturation, and the dehydrated gelatine was again soaked in a saturated solution of common salt in N/100 formic acid, to remove residual traces of sodium formate, while checking hydrolysis of the acid compound. The hydrochloric acid in combination with the gelatine was then determined by the Procter-Searle method. The acid gelatine was treated with 25 c. c. of N/10 sodium carbonate, evaporated to dryness, and gently ignited, with the usual precaution of washing out soluble salts after charring, and completing the destruction of organic matter by ignition, before returning the washings to the crucible, again evaporated to dryness and gently ignited, so as not to volatilise chlorides. The residue was then redissolved and titrated back with N/10 HCl and the loss of alkalinity calculated as HCl combined with gelatine; the sodium chloride being neutral, and the formic acid destroyed. I have described the method in some detail, as it is a very convenient one for the determination of acid in pickled pelts, which often contain large excess.

The results of four determinations were 1.044, 0.986, 0.903, and 0.988 milligramme-molecules per grm. of dry gelatine, giving an average of 0.98 mgr.-mols. per grm., or 3.58 per cent. of actual HCl on the gelatine. The fixed formic acid was not determined, but cannot have been large, as the hydrochloric acid found approached the maximum which could have been fixed.

had hydrochloric acid itself been used for swelling under the like conditions.

Experiments were also made with carefully delimed sheep-pelt similarly treated with formic acid and salt, with the result that four determinations gave 1.06, 1.12, 1.03 and 1.03 grm.-mols. of HCl per grm. of dry skin-substance, a result almost identical with that with gelatine.

The bearing of these experiments on several points of technical importance is obvious. It is clear that the advantages of Seymour-Jones' formic acid pickling process, apart from the antiseptic action of traces of formic acid and formates, consists simply in the avoidance of any excess of a strong acid, and that the same results would be attained in a cheaper way by preliminary treatment with a quantity of hydrochloric acid insufficient for complete pickling, and subsequently with saturated salt solution to which a small quantity of formic acid had been added. Perhaps about 3 per cent. of actual HCl on the dry weight of the skin, or say 2 per cent. of 30 per cent. hydrochloric acid on the wet pelt weight might be safely employed, with the addition to the final salt solution of 1 per cent. of formic acid on the dry, or one-fifth per cent. on the wet weight of the skins.

A mixture of sulphuric acid and salt may be substituted for hydrochloric. There is no question that the quantities of sulphuric acid commonly used in commercial pickling are greatly in excess of what is really needed. The writer once, through a clerical error, made an experimental pickling with one-tenth of the acid used by a very successful pickler, and the skin kept perfectly, and could be tanned without salt, or at least with a much smaller quantity that is usually required. Of course, if it is desired to substitute an organic acid, say formic, for the whole or a part of the mineral acid present in skins or leather, this is easily accomplished by treatment with the salt of an organic acid, and this method is perhaps the most effective means of securing the absence of "free" sulphuric acid in tanned leathers. It may be noted also that if a trace of an organic alkali salt, say sodium acetate, is introduced into a leather, it will not only neutralize any actual free mineral acid which may have been present, but will prevent any of our present analytical processes from detecting acid present as sulphonates, or mineral salts decomposable

by heat, which sometimes cause apparent "free" acid to be reported.

It may not be amiss also to remark that the same separation of mineral acid which has been described in the case of gelatine and pelt, may also occur in tanned leather, and it is most probable that if a leather acidified with organic acid were treated with sodium sulphate, "free" sulphuric acid would be found in the leather, although none had been employed directly in its manufacture.

THE PURIFICATION OF TANNERY EFFLUENTS.[1]

By F. P. Veitch.

INTRODUCTION.

One of the most important problems before the American tanner to-day is that of the proper purification of tannery effluents and the disposal of the by-products therefrom. The subject has received, during the past three or four years, a great deal of attention and it is not my purpose to go into details, as these can be had from authoritative works on the general subject of sewage disposal, of which there are a number of recent and excellent publications. Tannery effluent treatment is discussed also in the papers regarding the disposal of sewage at Gloversville, New York, where there are a great many tanneries and where the purification of the waste is largely a problem of the purification of the tannery effluent. A very good brief description of the installation is found in *Engineering Record,* Vol. 61, pp. 107, 157: 1910. Other papers on the subject are: Clark (41st Annual Report, Mass. State Board of Health, 1910); Morrison (*Journ. A. L. C. A.,* Vol. 6, 326); Alsop (*Journ. A. L. C. A.,* Vol. 7, 72); (Hein, et. al., Vol. 7, *Journ. A. L. C. A.,* 243, and Meunier, *Collegium,* No. 507, 268).

The chief materials in tannery effluents which should be removed are lime, dirt, dissolved hide substances, hair, tannin, acids, dyes, greases, dressing materials, chromium salts, sulphites and, last but by no means least, the micro-organisms which

[1] Read at the Ninth Annual Meeting of the *A. L. C. A.*, Washington, D. C., December 5, 1912.

some of the liquors contain in great numbers. The preliminary work for the installation of the sewage disposal plant at Gloversville, New York, which, so far as I know, is the most extensive work which has been done in this country on sewage containing tannery effluents, led to the conclusion that approximately half the weight of the hides and chemicals used in the making of leather at that point ultimately found its way into the effluent, the quantity thus lost being at the rate of 30,000 pounds per day, or 9,000,000 pounds per year. From the figures given in the report it appears that Gloversville sewage, which consists of about 26 per cent. of tannery effluent, yields approximately 2,200 parts per million of dry sludge. Morrison, in his article above mentioned, gives the quantity of suspended solids in tannery effluents at from 800 to 3,240 parts per million, with from 430 to 3,080 parts per million volatile, while in solution there are from 840 to 2,560 parts of total solids containing from 270 to 2,600 parts of volatile matter per million. Nailor, quoted by Morrison, gives from 820 to 1,280 parts per million of suspended matter, with from 110 to 1,000 parts of volatile material; and from 1,980 to 5,060 parts of soluble matter, with from 980 to 1,680 parts per million of volatile material. Meunier gives the total sludge from a sole leather tannery at approximately 0.11 per cent. of the effluent, or 1,100 parts per million, while the total solids, including the sludge and soluble matter, is given as 0.89 per cent., or 8,900 parts per million. Some figures on American sole leather tanneries have recently come into my hands, which show that the total solids per day from tanneries handling from 250 to 400 hides varies from 4,400 pounds to 7,330 pounds. Of these total solids, from 1,980 to 4,350 pounds are derived from the spent tan liquors, 600 to 1,540 pounds from the waste bleaches, and 380 to 860 pounds from the beamhouse waste. These solids are carried in the daily output of an effluent of from about 14,000 to 25,000 gallons per day. Of this effluent from 13,506 to 16,500 gallons is spent tan liquor, 2,600 to 8,400 is spent bleach, and from 1,280 to 3,280 gallons is beamhouse waste. Morrison estimates the effluent from a tannery handling 1,500 hides per week at approximately 25,000 gallons of old tan liquors, 10,000 gallons of lime liquors, 75,000 gallons puers and wash waters, 40,000 gallons of soaks; or a total of 150,000 gallons, or 25,000 gallons

per day for 250 hides. Meunier gives an effluent of approximately 16,000 gallons for from 110 to 120 hides per day. He shows that the greatest amount of total solids is contained in the waters from the beamhouse and machines, from working limed hides, from old limes, from the settling of the tan pits and from the waters used in the washing of the delimed hides in drums as well as from the liquors of the tan presses. The water drained from limed hides and the liquor from the tan yard, the washing of the tan pits and the water from scouring and finishing contain very little solid matter.

From these data it seems that the quantity of effluent to be purified and disposed of per day is from 8,000 to 15,000 gallons per hundred hides worked in daily, being proportionately somewhat less for multiples of 100 hides. Thus it may be said that the average effluent from a 250-hide yard making sole or harness leather will vary around 25,000 gallons per day.

How to handle this effluent, which is heavily charged with readily putrescible organic matter and with unlimited numbers of bacteria of all kinds, often with organisms producing extremely virulent diseases, is a problem which not only interests the tanner, but is often of vital importance to his neighbor and those living in the drainage area below the tannery.

Simple Methods of Low Efficiency.

Many tanners have attempted to solve this problem in simple and inexpensive ways, chiefly by running the tannery effluent through long troughs in which much of the solid matter which it carries settles out, then to large storage ponds where a great deal of bacterial purification, as well as further sedimentation, takes place. The freed effluent comes finally to the streams, where, while it is exceedingly objectionable, it is not nearly so objectionable as where a practice is made of running all of the waste into the streams. In this sedimentation or storage basin the effluent should lie for three or four days in order to permit as much settling as possible and as great a destruction of the organic matter in solution as the bacteria can accomplish in this time. The settlings must be removed from the troughs or settling basins periodically and the sludge thus obtained can be drained, and, if free of deleterious substances such as arsenic,

can be disposed of to the farmers, who use it for fertilizer purposes for which it is very suitable. The objection to this simple method of handling the effluent is, that it is inefficient as a means of purification and, further, the settling troughs and basins give rise to exceedingly objectionable odors which are particularly disagreeable if the tannery is situated in the neighborhood of a town. It is possible to purify further this partially purified effluent by chlorinating it as it runs from the settling tanks. This will result, if done properly, in a total destruction of the bacteria which the effluent contains, but will still leave in it the putrescible organic matter which is still particularly objectionable and which serves as an exceedingly suitable medium for promoting the multiplication of bacteria and other organisms in the stream into which the effluent flows. While these simple methods of purification result in improvement they are entirely inadequate so far as an acceptable purification of the effluent is concerned, and the tanner must look to other means for satisfactory methods of handling the effluent.

Methods Commonly Employed for Sewage Treatment.

Precipitation with chemicals, usually aluminum or iron sulphate; intermittent sand filtration, where sewage is allowed to stand in the filters for a period and the filters then rest for another definite period; contact beds, where the sewage remains in beds filled with small broken stone for a short time and is then let out with a brief intermittent resting period for the bed; sprinkling filters, where the sewage is sprayed on the surface of a deep bed of coarse material through which it passes; settling tanks, where sewage is simply allowed to settle for a definite period; septic treatment of sludge, where the sewage is retained in the filters long enough to insure its partial purification from organic matter and organisms by the bacteria contained in the filter; sterilization of the sewage with hypochlorites and running the sewage through fine screening, are the methods of treatment which are reasonably well established in the disposal of ordinary sewage. The above mentioned methods are named in order of their recognition in this country, and opinions as to the value of these practices are quite well established, especially as to the applicability of sprinkling filters, disinfecting methods, plain sedi-

mentation and treatment in two-story septic tanks. According to Fuller, chemical precipitation and broad irrigation processes are now rarely being installed in this country. The same is true of intermittent sand filters, while electrolytic treatment, strainers, slate beds, ozonization, and aeration have not become well established on a recognized basis. The efficiency of these practices in the purification of sewage is indicated roughly in the following table, taken from Fuller's "Sewage Disposal."

TABLE I.

EFFICIENCY OF SEWAGE PURIFICATION METHODS.

	Percentage Purification		
Method	Suspended matter	Organic matter	Bacteria
Fine screens (30-mesh or finer)	15	10	15
Sedimentation	65	30	65
Septic treatment	65	30	65
Chemical precipitation	85	50	85
Contact filters[1]	85-90	65-70	80-85
Sprinkling filters[1]	85-90	65-70	90-95
Intermittent sand filters[1]	95-99	90-98	98-99

These figures are a rough indication of what may be expected in the purification of sewage by the several methods mentioned. Fuller gives the rough approximate cost of treating sewage per million gallons by the several systems in Table II.

The cost of small installations will be proportionately somewhat higher, and the annual cost, independent of supervision, of operating works, to treat a million gallons per day exclusive of hypochlorite filters or sand filters, will range from about $600 with automatic control, contact beds, or sprinkling filters, to $1,500 or $2,500 for intermittent sand filters.

Dealing as they do very largely with the handling of tannery effluents, the conclusions and recommendations for the disposal of sewage at Gloversville are probably of more value than other American conclusions on the subject. They are:

1. The sewage of Gloversville is of such a character as to permit of successful purification by biological processes. The effect of the chemicals from the mill tanks, while doubtless di-

[1] The figures for the last three forms of treatment are on the assumption that the sewage is given some form of preparatory treatment before it is applied to the filters, and that with the sprinkling filters the effluent is allowed to settle.

TABLE II.

APPROXIMATE AREAS, COSTS, AND CAPACITIES OF WORKS FOR TREATING 1,000,000 GALLONS OF SEWAGE PER DAY (SEPARATE SYSTEM).

	Area	Capacity (gallons)	Cost
Grit chamber[1]	150 sq. ft.	750	$200-$500
Preliminary fine screens[2] (36 meshes to lineal in.)	400 "	—	4,000-5,000
Preliminary two-story settling tanks:			
Upper compartment	3,000 "	150,000-100,000	8,000-15,000
Lower compartment	—	—	—
Sludge drying beds (or filters) 1 ft. deep	3,500 "	—	600-1,000
Intermediate fine screens	400 "	—	4,000-5,000
Roughing filters	350 "	—	2,000-3,000
Intermittent sand filters	17 acres	—	8,500-85,000
Contact filters (5 ft. deep)	1.7 "	—	22,500-60,000
Sprinkling filters (6 ft. deep)	0.5 "	—	15,000-25,000
Final settling tanks	1,000-2,000 sq. ft.	75,000-100,000	5,000-10,000
Hypochlorite treatment	400 "	—	1,000-3,000
Final sand filters	2 acres	—	1,000-12,000

minishing the efficiency of the germs, does not prevent their carrying out their work to completion.

2. The winter climate at Gloversville is very unfavorable to biological processes of purification, and while it may be possible to operate the plant without protection from the cold, the success of such an undertaking appears to be somewhat doubtful. If the filters should be covered there would be no doubt about their successful operation during the winter.

3. The sewage can be purified at the rate of 1,000,000 gallons per acre upon sprinkling filters in spite of the chemicals in the sewage, its strength and the low temperature during the winter months.

4. It has been demonstrated that in some cases it is possible to remove over 90 per cent. of the suspended matters in the mill wastes by means of small tanks located at the mills. Such a degree of efficiency would permit all tank effluents to fall within the limit of 300 parts per million of suspended matter, which

[1] Not needed for separate sewers.

[2] Fine mechanical screens not now made smaller than for 5 million gallons. Filter areas are net effective surface; all others are gross building areas.

may be taken as a fair, though perhaps under local conditions, a rather high standard.

5. With sedimentation as a preparatory method of treatment, about 7 cubic yards of sludge will be produced per 1,000,000 gallons of sewage. This quantity may be reduced by allowing the sludge to accumulate in the settling tanks and undergo more or less decomposition, thus virtually changing the method to the septic process. The reduction which could be effected in this way would amount to approximately 30 per cent. To this quantity of sludge produced by preparatory sedimentation should be added that produced by secondary sedimentation of the filter effluent, which will amount approximately 3 cubic yards per 1,000,000 gallons of sewage treated, making a total of approximately 10 cubic yards per 1,000,000 gallons.

6. No incrustation has been discovered upon the surface of the filtering material due to lime and other chemicals present in the sewage.

7. The coloring matter in the sewage is of such a character that it is partly removed during its passage through the settling or septic tanks, and generally entirely removed by the time it has passed through the sprinkling filters. Occasionally the color may make its way through the sprinkling filters, but in all cases it is entirely removed by the time it has passed through the sand filters.

8. More or less odor must be expected in the vicinity of the plant, especially around the sprinklers. This odor will resemble that of tannery wastes, and will not be of a putrefactive and highly offensive nature.

Recommendations: After giving the entire problem most careful consideration, and in light of the various studies and experiments, the following recommendations were made:

That sedimentation be adopted as a preparatory method of treating the sewage.

That the effluent from the sedimentation process be filtered through sprinkling filters either 7 or 5 feet in depth at the rate of 1,000,000 gallons per acre per day.

That the effluent from the sprinkling filters be passed through secondary sedimentation basins sufficient in capacity to reduce the quantity of suspended solids to 30 parts per 1,000,000.

That if the filters are constructed 5 feet in depth the effluent from secondary sedimentation basins be filtered through sand filters at the rate of 1,000,000 gallons per day.

The methods based on the aeration or ozonization of sewage have apparently not been worked out to a satisfactory basis. While both of the practices destroy much organic matter which is in solution, and while ozonization especially may free the sewage almost entirely of bacteria, it is still heavily contaminated with organic matter, the removal of which requires a subsequent passage through some form of filter bed. It should be pointed out, however, that aeration plays a very important part in purification with sprinkling filters.

Sprinkling filters provide for the application of sewage in a comminuted form, usually as a spray, to fairly thick layers of coarse material resembling in size that of contact filters. In accomplishment they also resemble contact filters as distinguished from sand filters in that the effluent is non-putrescible, although by no means free of suspended matter, bacteria or organic matter. Essentially this type of filtration is applicable for the elimination of nuisances due to decomposition of organic matter in sewage rather than to the substantially complete removal of objectionable bacteria. For the latter purpose they are of use and can be supplemented by combination with other methods.

The capacity of sprinkling filters to purify sewage depends upon the strength of the sewage, the size and depth of the filtering material, and the quality of effluent which it is desired to secure, particularly in the winter in severe northern climates. The Columbus, Ohio, plant has a capacity of 2 million gallons per acre daily, with an effective depth of 5 feet. At Baltimore, with a depth of 9 feet and size of stone of 1-2½ inches, an average rate of 2½ million gallons daily is provided for.

Fuller has recently adopted the practice of specifying an average depth of 6 feet for the filter and an average rate of 2 million gallons per acre daily. The present tendency, while the average depth is 6 feet with a rate of 2 million gallons per acre daily, is to increase the rate for deeper filters and weak sewage, but to

decrease it to offset the influences of winter weather, trade wastes, street wash, etc.

As compared with contact filters, it may be said that sprinkling filters give approximately equal efficiency with a rate of filtration 3-4 times as high as prescribed for contact filters. This seems to be explained by the benefits resulting from the aeration of the influent and the constant providing of oxygen within the filter. Experience has also shown that the filter requires very infrequent cleaning, and a minimum of attention. On the other hand chemical precipitation requires close attention and must be followed by filtration. Sand filters readily become choked if dosed with raw settled sewage and require frequent cleaning. Contact beds have a smaller capacity and no greater efficiency.

The systems of dealing with tannery effluents abroad may be classed under two heads, (1) mechanical and mechanico-chemical and (2) oxidation and biological methods. Tannery effluents are nearly always treated, before filtration, with ferrous sulphate, iron, alum or aluminum salts or with peat, to assist sedimentation, and are then filtered through sand and finally through clarifying towers, basins or wells. The process of this kind most in use in Germany is that of König and Degener, in which peat is employed in a finely divided state, and also lime, iron or aluminum salts. A clear, colorless and odorless filtrate is obtained which may be discharged direct into the stream. One to two kilos of peat and 100-300 grams of iron salt are required per cubic meter of water. Kratschmer's process consists in treating the waste water, which generally contains free lime, with aluminum sulphate and filtering through sawdust, coke or sand. If arsenic be contained in the water, it is treated with ferrous sulphate and milk of lime and allowed to settle for 24 hours. Soaks and washing waters are filtered through a layer of spent bark 2-3 feet thick and deodorized and disinfected by the addition of chloride of lime or calcium bisulphite. Spent tan liquors are treated with lime or filtered through sand or porous earth. Of the oxidation or biological processes that of Dunbar is used to the greatest extent in German tanneries, but these processes can only be used when the amount of mineral matter present is low.

Suggestions as to Methods to be Employed.

Careful consideration of what has been accomplished in the way of sewage purification and disposal seems to warrant the opinion that technically the purification of tannery effluents presents no great difficulty, though it must be said that the cost of doing this will often be considerable. I have reached the conclusion that where space is restricted, land values high, or where in thickly settled communities the presence of the odors would be especially objectionable, that sedimentation or centrifuging of the mixed tannery effluent followed by passing it through a sprinkling filter, then a settling tank, and finally through a sand filter, as recommended by the engineers for the Gloversville installation, will give entirely satisfactory results and be unobjectionable. Less desirable methods would be to treat the effluent from the sprinkling filters with hypochlorite which would complete its purification from bacteria, leave in but little organic matter, which is non-putrescible, and would add to it chlorine against the presence of which in river waters much can be said. Or, less efficient and desirable still, the settled sewage may be treated with hypochlorite which will leave in the effluent much putrescible matter to contaminate the drainage waters below the tannery.

Crude sewages require from 4 to 12 parts per million of available chlorine; septic effluent from 10 to 15 parts and sprinkling filter effluents from 3 to 4 parts per million of hypochlorite of 33 per cent. available chlorine; 25 pounds of commercial bleach per million gallons. These doses will remove from 95 per cent. to 99 per cent. of the bacteria present. The time of contact should be at least 15 minutes and 30 minutes is somewhat preferable. If longer periods are available the dose may be reduced somewhat.

Where space is ample, land values low, and the country thinly populated so that odors which will result will not be strenuously objected to, sedimentation and sprinkling filters, to be followed by broad irrigation, is probably the best and cheapest way of handling the effluent. Less desirable methods would be the treatment of the sprinkling filter effluent with hypochlorite as mentioned above.

It will be seen from the figures in Table II above, that the cost of these installations and their operation is not at all prohibitive. While the cost of efficient installations is of course high, it would be well for the tanning industry to resign itself to this expense as soon as possible, as the industry not only owes it to itself but to the country at large to eliminate this nuisance. If the tanners do not themselves take the initiative it is not at all unlikely that the cost then resulting will be greater than if the industry had itself attended to the matter.

Disposal of Sludge.

One of the most annoying problems in connection with the purification of sewage is the disposal of the sludge which is obtained from the settling tanks, or from the filter beds. It is quite customary either to dump this highly putrescent matter on waste lands, to bury or burn it, or to give or sell it to farmers. The dumping and burying, while among the most economical ways of disposing of the sludge, are highly objectionable. The disposal of the waste sludge to farmers is advisable where it can be practiced, but often this is not possible. Where this wet sludge can be disposed of to farmers regularly, particularly where the quantity does not exceed one ton of air dry sludge per day, this procedure is probably the most economical and profitable method of disposing of it. The average cost of the various systems of disposal of sludge containing 90 per cent. water is estimated to be: Covering land, 4 cents; dumping at sea, 10 cents; trenching in soils, 10 cents; pressing less than 10 cubic yards per day, 12 cents; pressing and burning, 36 cents.

Where the quantity of sludge exceeds one ton of dry material per day, however, it is doubtful if it can be regularly disposed of in this way and some other more suitable methods should be adopted. By filter pressing or centrifuging the sludge, the moisture which was formerly between 80 per cent. and 90 per cent. is reduced to about 60 per cent. Wet sludge pressed is reduced four-fifths in volume and the amount of water to from 50 to 60 per cent. This is less putrescible than the wet sludge, has much less odor, and can be shovelled readily. Filter presses are used for pressing sludge, the pressure used being about 60-75 pounds per square inch and lime to the extent of from 3-7 per cent. of

the weight of the sludge is added before the sludge is pressed in order that it may be made to give up the water more readily. The cost of sludge pressing in England is from 50 cents to $1.25 per ton of pressed cake, in the United States from 75 cents to $1.50.

Centrifugals for drying sludge have been recently used in Germany and the sludge thus dried contains from 50 to 75 per cent. water and lime need not be used before centrifuging. The cost of drying is given as from 5-7 cents per cubic yard of sludge treated. The sludge thus produced may be burned in a destructor or may be further treated and used as a fertilizer. Sludge may be burned when it does not contain more than 60 per cent. of moisture. At Worcester, Mass., experiments were conducted in burning sludge and the cost was approximately $3 per ton of dry sludge. In other experiments in England the cost of burning the sludge was 63 cents per long ton. The pressed or centrifuged sludge, as above stated, can be burned under the boilers and thus finally disposed of in an unobjectionable manner. The material contains on a dry basis approximately 50 per cent. of volatile matter. The nitrogen runs from 1 to 3 per cent., lime from 2 to 20 per cent. and phosphoric acid from ½ to 2½ per cent., while grease may run all the way from 2 or 3 per cent. to 10 or 15 per cent. This dried material is valuable for fertilizer purposes, not alone because it contains valuable fertilizer material, but because it will serve as a filler and dryer, of which large quantities are consumed annually at from $2 to $4 per ton. It is quite certain, therefore, that where the supply of this dried sludge is considerable, it can be disposed of at from $2 to $5 per ton to fertilizer manufacturers. From published figures on the subject it seems that wet sludge may be pressed at a cost of from $1.20 to $2.85 per ton of dry material, while it may be centrifuged at from 30 to 60 cents per ton for the centrifuged material. This pressed or centrifuged sludge, containing approximately 60 per cent. of water, may be then dried in rotary dryers with waste steam at a cost of approximately 50 to 75 cents per dried ton. In other words, the cost of centrifuging and drying the sludge should probably not exceed $1.50 per ton, and can possibly be done for less. This dried material, containing approximately 50 per cent. of volatile matter, and from 1 to 3 per cent. of nitrogen, should bring the tanner from $2 to $5 per ton in bags, and

while there may be no great profit in it, it seems reasonable to think that its disposal in this way would at least pay for its handling and eliminate the objectionable features obtaining in other methods of disposal.

DISCUSSION.

In answer to a question, Mr. Veitch said that it was probable that on an average the dried sludge could be sold at a price which would pay for treating it, but not for enough to cover the whole cost of disposing of the tannery sewage.

Several members expressed the opinion that the estimates in Mr. Veitch's paper in regard to the quantity of effluent discharged by tanneries are much too low. Instead of 100 gallons per day per hide, Mr. Oberfell had found more than 300, Mr. Morrison 500, Mr. Smoot from 300 to 375.

Mr. Wallin said that the city of Grand Rapids draws its water supply from a river which only three miles above the intake receives the effluent from a large tannery. Examination of the water by experts showed that there was no contamination dangerous to the health of the city. The stream in this case is a very large one, but the color of the tannery waste shows for a mile below the point of discharge.

SALT STAINS.[1]

By John H. Yocum.

A stain varying from a rusty red to a dark brown occurs frequently on leathers, more pronouncedly on vegetable than on chrome tannages. It has been found that this stain shows on the pelt after dehairing, and since these stains do not develop in fresh pelts, the origin is then without doubt in the curing of the pelt. This stain is more pronounced on pelts remaining in a salt cure for a long time than in those cured for a short time. The commercial importance of this matter is that light colored leathers are the most valuable, and because of this stain many pelts are put into black leather which otherwise would go into the lighter shades; and also heavy leathers are decreased in value because of it.

[1] Read at the Ninth Annual Convention of the *A. L. C. A.*, Washington, D. C., December 5, 1912.

The character of the salt used and the period at which the salting is done have an influence on the formation of the stain. Pelts salted during the winter months with clean salt seldom have this stain, while pelts salted during the summer months with clean salt frequently do have it. It is evident from this that the cause of the stain is not entirely dependent upon the salt, but primarily is due to some change in the constituents of the pelt itself. These stains occur most frequently at the bend of the pelt in the pack where the air can best reach the pelt. When salt that has been previously used, dirty salt, salt containing iron, and some of the denatured salts, are used, more of the stain obtains on the leather than does obtain when the pelts are salted with fresh, clean, evaporated salt. Pelts once packed, then taken up and repacked, are almost always stained, even where the greatest care is taken in the quality of the salt used for repacking.

The usual process of curing is effected in this country by placing the pelt immediately after coming from the animal and after being hosed down and selected, into a conveniently sized pile, flesh up, ordinarily containing from 600 to 1,000 hides according to their weight. Over each pelt is distributed about 25 per cent. of its weight of salt, the edges of the pile being kept slightly higher than the center, and uniform in height by turning back the pelts at the edge and making a fold. Hides require at least four weeks to cure properly, skins a less time. In the winter months the hides and cellars are cooler than during the summer months. Sometimes hides remain in these packs six months or longer, in which case they are usually badly stained. Frequently with denatured salt the stain appears on the flesh, but in such cases little damage results to the leather. Generally the stain is just under or on the grain or hair side of the pelt and does not penetrate further than the epidermis, seldom appearing clear through the pelt.

When the pelt is unhaired, these stains show up pronouncedly, and by moistening a piece of filter paper with strong acetic acid and placing it over the stain on the unhaired pelt, ordinarily the paper when removed gives a reaction for iron. Frequently by pursuing this same test on leather showing the stain, the reaction for iron can be obtained, but no test for iron can be obtained where in either case no stain appears. Analysis of the raw pelt

uniformly shows iron in its ash. Analysis of the tanned leather shows iron in the ash where stains exist, but no iron where they do not exist, or at least only as a trace. Wide differences can exist in the quantity of iron found in the ash from two different raw pelts of like character, which if tanned without salting, will not show in either case these stains in the resulting leather.

From these facts it would appear that the source of the stain is inherent in the pelt itself and that iron is generally associated with it; it follows that the iron of the stain in the leather exists in some chemical condition in the raw pelt different from the iron in that portion of the pelt which has not been stained, and that the conditions favorable for the change from unstaining iron to staining iron are time, dirty salt, warm cellars, improper cooling and improper washing of the pelt, and impurities in the salt such as iron and some denaturing materials.

It is superfluous for me in making this report to add to what Dr. Abt and Professor Becker and Professor Paessler have done in this connection in (1912) 388 and 408-418 *Collegium*. From their work it is quite evident that the cause of salt stains in France and Germany is considerably obscured by the fact that either denatured salts are used or there is a lack of salt; both these conditions being brought about by the fact that salt for hides is so expensive for one reason or another that it is not used in sufficient quantity to perfectly cure the hide. It would seem that in one case the denaturing of the salt occasioned stains, and in the other case, that a lack of salt probably permitted the improper cure of the hide, occasioning bacteriological transformations that subsequently resulted in staining, which would not have occurred had sufficient salt been used, properly to dehydrate the pelt.

It would seem that a salt, therefore, which would prevent salt stains needs to have something in addition to ordinary sodium chloride which would prevent these defects in the cure of the hide, and to prevent these defects, the salt used for curing should have the following characteristics generally:

1. It should be a denatured salt, not capable of being used for edible purposes, and should be of such a character as to be accepted by the Governments where commercial salts are not subject to duties, while edible salts are.

2. It should be germicidal enough to prevent the growth of bacteria, which may possibly form chromogenic products and cause other changes due to enzymes, as well as germs.

3. The conditions under which salting is conducted should be such that with clean salt, the hæmoglobin or oxyhæmoglobin will not be changed into hæmatin, which acts as a tanning agent and fixes the iron as an organic compound to the hide or gelatine of the skin, subsequently causing the stains so-called.

The fact that the improper removal of the blood by washing or otherwise has a great influence on the formation of salt stains, as they are known in the United States, has not been given sufficient consideration. In experimenting along this line, I have tanned out skins with hæmoglobin and I have generally found that under conditions where these skins being saturated with hæmoglobin and have subsequently been salted with pure salt, that they developed on tanning, stains akin to salt stains. By following the same procedure with phosphate of soda and with calcium sulphate, in the salt, much the same conditions have resulted.

I therefore conclude that so far as relates to properly drained (free from blood) skins, the stain resulting therefrom will be due to the salts used. Dr. Abt states that the phosphoric acid of the nuclein combines under certain conditions, forming phosphates and fixing the iron of the blood remaining in the skins. Notwithstanding this, I have never seen stains in roans which had been pickled with sulphuric acid and salt, and then dried out; in fact there was only a very small trace of iron in these skins. With skins treated with hæmoglobin and pickled by the customary method, it was not difficult to obtain stains.

It is rather indicated to me from the work that I have done in this connection, that the stains spoken of by Dr. Abt and Professor Becker are the results rather of improperly cured skins, or the result of the use of denatured salt, or skins improperly prepared for salting. I would conclude that the salt stains known in the United States and probably in Canada are wholly due to the action of the hæmoglobin; its decomposition product, hæmatin, being a tanning agent upon the fiber and gelatine of the skin. In this country, salt is not denatured, nor is there a disposition to under-salt skins; therefore it is evident that the chief cause of

stains is the improper washing out of the blood, or the use of too high a temperature during curing.

One would judge that in the United States a material should be used which, for the obviation of this nuisance, has the characteristics, of first, a deoxidizing agent; second, an alkali; third, an antiseptic; and fourth, assists in the cure. The reason that it is necessary to deoxidize is that the hæmoglobin absorbs oxygen, changes to hæmatin, and fixes itself to the hides as a tanning agent; consequently a deoxidizing agent will absorb the oxygen and prevent the change of the hæmoglobin into hæmatin. It has been shown by certain German concerns that the use of an alkali assists in the solution of the blood and permits it to drain from the hides and skins better than it ordinarily would. It is a well established fact that alkaline conditions of the blood make it more soluble than acid conditions do, consequently for a proper drainage it is necessary to have an alkaline condition of the salt used. From Dr. Abt's and also from Professor Paessler's articles, it is apparent that where the skin is not completely salted or cured by salt, bacterial colonies may form which may ultimately attack the hair follicles destroying them to such an extent as to allow of chromogenic colorations following the action of some of these bacteria.

A proper cure with a proper salt with sufficient alkali will obviate all these objections, that is, a cure of 30 days with a salt that,—

First. Will prevent the oxidation of the hæmoglobin into hæmatin, which causes a localized tannage of iron.

Second. Contains the elements which will permit the proper drainage of the blood from the hide, because of its alkalinity.

Third. Is germicidal enough to prevent the growth of bacteria which are dependent upon the soluble gelatines in the presence of sodium chloride for their life history.

Fourth. Admits of the proper cure of the skins.

Fifth. Is not too expensive for commercial use.

Summarizing the above facts, it would appear that so far no proper denaturing material has been used or devised for the purpose of preventing edible salt being used for salting hides in certain countries in Europe. This of course is of importance to us,

in that we are importers of the hides resulting from this treatment, and the hides must be treated here in the soaks and limes without detriment. It has been proven by Dr. Abt and others that hides suffer from salt stains because of bacteriological action which we can only conclude is the result of either improper salting, or salting under conditions of quantity of salt and temperature which do not permit the proper cure of the skins.

It must be allowed that in the United States, where sufficient salt is ordinarily used, the conditions of the preliminary washing of the hides have a great deal to do with the resulting stain and can be obviated by a proper salt which will make more liquid the blood, and prevent the fixation of the iron as hæmatin, temperature, time and conditions generally being considered. Any agent which will prevent salt stains under the best conditions of time, temperature, etc., must be sufficiently strong to allow the average small packer to so cure his hides as to prevent salt stains because his hides remain in pack longer than is normal with the larger packer.

I would therefore advise that this Association consider the importance of obtaining some agent which will meet these requirements, and will be available commercially for general use. It would appear to me that this is of more importance to the tanner than it is to the packer, consequently if the National Tanners' Association does not take the matter up, it is hopeless for any one of us to attempt to get the packers to adopt a method for the prevention of salt stain, which may cost them a cent or two more per hide than their present methods of salting.

DISCUSSION.

H. C. Reed said that he had occasion recently to look for the cause of some bad stains on leather. Examining the packs from which the hides had been taken, he found on the hides a substance supposed to be salt. It was slightly damp, black, and imbedded in the flesh side. In drying it became grayish, and gave the following analysis: Sodium chloride, 14.74 per cent.; calcium sulphate, 30.51 per cent.; calcium carbonate, 25.61 per cent.; iron and aluminum oxides, 2.52 per cent.; silica, 23.30 per cent.; water, 1 per cent.; organic matter, by difference, about 32 per cent. The substance was apparently uniform in composition, and cut like cheese. Mr. Reed expressed the opinion that the sub-

stances found were present in the original salt. Attention was called to the fact that Dr. Abt claims that the presence of calcium sulphate in the salt is a determining factor in a large class of salt stains.

Mr. Morrison coincided with Mr. Reed's opinion that the substance in question was mined with the salt. He further suggested that one cause of stains is the manure which is left on when the hides are salted, and said that if the packers could be induced to cleanse the hides of blood and filth much of the trouble would be avoided. Clean hides salted with clean salt seldom show stains.

V. A. Wallin asked Mr. Yocum whether any conclusion had been reached in regard to the kind of salt which should be used to prevent stains. In reply, Mr. Yocum said that the requirements are clear, but that so far as he knew the proper material has not been found. Mr. Wallin said he thought that the National Association of Tanners would gladly undertake to finance an investigation of the subject, and that the packers would come into line without trouble, since they are also tanners and interested in preventing salt stains.

W. H. Teas asked whether the packers use fresh salt every time. Mr. Wallin thought they claim to do so. Mr. Yocum thought it impracticable to prevent the use of salt which has been brushed off and swept up and washed.

Mr. Griffith asked whether Mr. Yocum's results confirmed Dr. Abt's conclusions in regard to calcium sulphate as the cause of salt stains. Mr. Yocum said they did. The hæmoglobin of the blood is changed by catalysis into hæmatin by impurities in the salt.

THE DETERMINATION OF ALKALINE SULPHIDES.[1]

By Douglas McCandlish, B. Sc., and John Arthur Wilson.

In a recent article on the determination of sulphides in lime liquors, Messrs. J. R. Blockey and P. V. Mehd (*Journal of the Society of Chemical Industry,* April 30, 1912, No. 8, Vol. XXXI, and reprinted in this JOURNAL, Vol. 7, page 358) drew

[1] Read at the Ninth Annual Meeting of the *A. L. C. A.*, Washington, D. C., December 5, 1912.

attention to inaccuracies in the method of Procter (Leather Industries Laboratory Book, pp. 55, 87) and proposed to replace the zincammonium sulphate used in the latter method by a zinc sulphate solution containing ammonium chloride. Whilst experimenting with the method, we noted some points, not mentioned in the above paper, which we believe to be worthy of consideration.

With the standard zinc solution which they recommend, Blockey and Mehd apparently obtained the same result for a given amount of sulphide, both in pure aqueous solution and in a saturated solution of calcium hydrate. Although their method is not described in detail, we have tried to follow it as closely as possible. The results of these first experiments are given below. The sulphide solutions were titrated with a N/10 solution of zinc sulphate, to which had been added 50 grams of ammonium chloride per liter. A 0.2 per cent. solution of sodium nitroprusside was used as an external indicator on a spot-plate. It should be mentioned that the lime used for making the lime water solution was obtained by strongly heating precipitated calcium carbonate. "Merck's" sodium nitroprusside was used as indicator. It is well to remember that dilute sodium sulphide solutions are somewhat unstable and lose H_2S on standing. It is necessary, therefore, to standardize the sulphide solution frequently. This may be conveniently done by means of iodine solution, or by the usual gravimetric method.

TABLE I.

	No. cc. N/10 $ZnSO_4$ + NH_4Cl required	Error per cent.
5 cc. N/50 Na_2S solution in 25 cc. H_2O..	0.7	30
10 cc. N/50 Na_2S solution in 25 cc. H_2O..	1.4	30
15 cc. N/50 Na_2S solution in 25 cc. H_2O..	2.1	30

Although the method of Blockey and Mehd deals particularly with sulphides in lime liquors, it is interesting to note that, in pure aqueous solutions, where low results were obtained, there was a considerable evolution of hydrogen sulphide. Since H_2S does not produce any color with sodium nitroprusside, it naturally follows that, in nearly neutral solutions where hydrogen sulphide is formed by hydrolysis, the results will be low. This difficulty can be overcome by using an alkaline standard solution.

If some of the standard zinc solution used in the above ex-

periments be added to a clear, saturated solution of calcium hydrate, there will be a distinct precipitate of zinc hydrate. This proves quite conclusively that the amount of free ammonia formed by the interaction of the lime and ammon. chloride is insufficient to prevent the precipitation of zinc hydrate. This fact is further borne out by the results in the following table:

TABLE II.

	No. cc. N/10 $ZnSO_4$ + NH_4Cl required	Error per cent.
5 cc. N/50 Na_2S solution in 10 cc. saturated $Ca(OH)_2$ solution	1.0	0
5 cc. N/50 Na_2S solution in 25 cc. saturated $Ca(OH)_2$ solution	1.2	20
5 cc. N/50 Na_2S solution in 50 cc. saturated $Ca(OH)_2$ solution	1.3	30
5 cc. N/50 Na_2S solution in 75 cc. saturated $Ca(OH)_2$ solution	1.35	35
5 cc. N/50 Na_2S solution in 100 cc. saturated $Ca(OH)_2$ solution	1.4	40
5 cc. N/50 Na_2S solution in 150 cc. saturated $Ca(OH)_2$ solution	1.4	40

Larger amounts of N/50 Na_2S solution gave results similar to those in Table II.

The above table shows that the error increases with increasing concentration of the lime solution. The first result in the table, which appears to be correct, is probably formed by a compensation of errors. As the solution becomes more dilute, greater quantities of sulphide are lost by the formation of hydrogen sulphide. The odor of this gas was quite distinct in the solution which gave an apparently correct result. The tendency to form a low result by the evolution of hydrogen sulphide was balanced by the tendency to form a high result by the precipitation of zinc hydrate.

The solution in question has two disadvantages: it is not sufficiently alkaline to prevent a loss of hydrogen sulphide, formed by the hydrolysis of sodium sulphide in aqueous solution, and it does not contain sufficient ammonia to prevent the precipitation of zinc as a hydrate in lime solutions. The former disadvantage might be overcome by using lead acetate as an indicator, but sodium nitroprusside is generally preferable, and it would be better, if possible, to resort to other means of overcoming the

difficulty. This latter indicator not only gives a sharper and more satisfactory end point than does lead acetate, but also enables one to complete a titration in much less time. The other means is to use an alkaline zinc solution.

The second difficulty could be overcome by using a sufficiently strong alkaline solution. Here there are two possibilities: to have the zinc in the form of a zincate, such as sodium zincate (Na_2ZnO_2), or a zincammonium compound. In order to form sodium zincate in a solution of the necessary strength, such a large excess of alkali is required that the sodium nitroprusside is decomposed, thus rendering the end-point most indefinite. If an insufficient amount of alkali is used, zinc hydrate is precipitated. Hence this solution is impracticable.

The zincammonium compound is not without its objections. If the compound is made by adding ammonia to a solution of zinc sulphate until the precipitate, which at first forms, just redissolves, it will give a precipitate of zinc hydrate upon addition to a clear, saturated solution of calcium hydrate. This means that it would give abnormal results when used to determine sulphides in lime liquors—as observed by Blockey & Mehd. But as the amount of ammonia is increased, the tendency of a precipitate to form decreases. The error gradually decreases, but suddenly begins to increase, without having disappeared entirely.

This last difficulty was rather unexpected, but can be satisfactorily explained by the ionic theory. The zincammonium compound has the formula $Zn(NH_3)_4(OH)_2$. It is formed by the union of free ammonia with the zinc ion. This union is governed by the equation

$$\frac{C_{Zn^{++}} \times C^4_{NH_3}}{C_{Zn(NH_3)_4^{++}}} = K.$$

The zinc ion is the active factor in precipitating ZnS, as the zincammonium ion is not precipitated by soluble sulphides. An addition of ammonia to the zinc solution increases the value of the numerator of this equation. In order to maintain the required equilibrium, the denominator must also increase, but this can be effected only by the union of the ions in the numerator. By increasing the concentration of ammonia we can remove the zinc ion to an almost unlimited extent. This can be shown by

adding a great excess of concentrated ammonia to some of the standard zinc solution and then adding a small amount of a solution of sodium sulphide. There will be no precipitate, owing to the absence of sufficient zinc ions. But if this solution is now diluted, zinc sulphide will precipitate out, because the zinc ions are again liberated. Too great an excess of ammonia, as well as too little, gives abnormal results.

We now have the general properties of the required solution. It must be sufficiently, yet not excessively alkaline, and must have sufficient, yet not a too great excess of ammonia. If enough ammonia be added to prevent the precipitation of zinc hydrate, there will be enough present to remove some free zinc ions from solution, so that with all concentrations we are sure to obtain abnormal results in saturated lime water. But if just enough ammonia be added to prevent the precipitation of zinc hydrate, no error can result from that source and only a minimum error will result from removal of free zinc ions. This solution gives correct results with aqueous solutions of sulphide. It is not an ideal solution for use with lime liquors, but has one great advantage over the solution containing ammonium chloride. It gives the same result for a given amount of sulphide with widely different concentrations of calcium hydrate, whereas the solution containing ammonium chloride gives very different results. Since it is sometimes necessary to dilute the solution to be analyzed, for reasons which we shall mention presently, this fact favors the ammoniacal solution. The ammoniacal solution just mentioned does give high results with lime water, but the error appears to be a constant. Such a solution might be standardized to give correct results in lime solutions and so be made to serve its purpose as well as if it were an ideal solution.

One more difficulty now presents itself. In strong solutions of sulphide, abnormal results are obtained when using either the ammonium chloride or the ammoniacal zinc solutions. The reason for this is that a colored compound is formed by the interaction of zinc sulphide (removed from the titrating flask on the glass rod) with the sodium nitroprusside, even after all the soluble sulphide has been precipitated. This color finally disappears when a sufficient excess of the zinc solution is present, probably due to the repression of the slight ionization of the

zinc sulphide by the excessive amount of zinc sulphate. This can be demonstrated as follows: Equal volumes of sulphide solution are taken. To one is added slightly more than enough zinc sulphate to precipitate all the sulphide and to the other is added a large excess of zinc sulphate. Some of the sodium nitroprusside solution is now added to both flasks. In the former the precipitated sulphide will assume a reddish color while in the latter it will be unaffected.

Since this trouble is not appreciable in solutions of sulphide of a concentration of less than N/60, the solution must be diluted until such a concentration is obtained. With solutions stronger than N/60, 25 cc. of the solution should be titrated to completion. Another 25 cc. of the solution should then be taken and an amount of water added equal to five times the amount of N/10 zinc solution required for the first titration. This diluted solution gives no appreciable error.

A longer, but possibly more satisfactory method is to titrate 25 cc. of the strong solution to completion. To another 25 cc. of the solution add three-fourths of the amount of zinc solution required for the first 25 cc. Then dilute the solution and precipitate to 100 cc., filter, and complete the titration with 25 cc. of the filtrate. Multiply this last result by four and add it to the result obtained for the first three-fourths of the solution.

In view of the foregoing facts, it will be seen that neither the addition of ammonium chloride nor of ammonia to zinc sulphate furnishes a solution which gives correct results under all con ditions. We trust, however, that our experiences may be of some use to those who are working along these lines to obtain an ideal solution.

THE GEOGRAPHIC DISTRIBUTION OF TANNIN PLANTS.[1]

By W. W. Stockberger,

Bureau of Plant Industry, U. S. Dept. of Agriculture.

The constant increase in the quantity of tanning materials which is being imported into the United States cannot fail to arouse further interest in the source of these products and in the

[1] Read at the A. L. C. A. Convention, Washington, Dec, 5, 1912.

economic conditions prevailing in the countries from which they are derived. Since in recent years important additions have been made to the number of plants recognized as available sources of tannin, further knowledge regarding their abundance and general region of occurrence is naturally very desirable. Also much more definite information is needed concerning the local distribution and commercial range of all important tannin plants before either their economic significance or their practical importance as an available source of tannin for trade uses can be fully determined.

The limits of this brief and general paper will permit the mention of only a few of the salient features of the distribution of tannin plants, with very little discussion of this subject in its practical aspects, although the latter are yearly growing in importance. The significance of certain facts respecting the geographical distribution of tannin plants can perhaps be more fully appreciated if some consideration is first given to the distribution of tannin in the various natural orders and families into which plants have been grouped with respect to their relationships. This is a subject which has received very little attention except for the contribution of Dr. Dekker[1] in his invaluable monograph on the tannins, which has been freely drawn upon in the preparation of this paper. In Dr. Dekker's work the results of his own extensive researches are so combined with those recorded in the widely distributed literature of the tannins that the whole presents a mass of data from which important generalizations may be made. However, since the number of plants in which the presence or absence of tannin has been determined is relatively small in comparison with the number of known species of plants, it is very probable that these generalizations will be more or less modified by future investigations.

When the groups or subdivisions into which botanists divide the plant kingdom are considered with respect to the occurrence of tannin therein it appears that some forms of this compound appear in all of the main groups of plants, but that in every group there are many families that contain little or no tannin. In the lower groups of plants represented by the algæ, fungi and lichens, tannin is of frequent occurrence but owing to the rela-

[1] Dekker, J., "De looistoffen," Bulletin van het Koloniaal Museum te Haarlem, No. 35, 1906.

tively small mass of plant material furnished by these groups the total quantity of tannin produced is not sufficient to have any commercial importance. In the next group, the mosses, very few plants have been found which give a positive reaction for tannin. The group which includes the ferns has numerous species which vary in tannin content from a mere trace to as much as 10 per cent., but it is in the higher group of seed-plants that tannin occurs most abundantly.

The subdivision of seed-plants, known as the Gymnosperms, contains a large number of plants which have a high tannin content. The most important of these are species of trees such as the pine, hemlock, spruce and fir. On the other hand among the Monocotyledons the number of families in which tannin has been found is small, and of these the Palmæ is the only one in which there are plants which furnish tannin in commercial quantity. Among the hundreds of species of the families which include the grasses, sedges and lilies, the occurrence of tannin even in very small quantities is quite rare.

The last and most important division of the seed-plants, the Dicotyledons, furnish by far the largest number of plants rich in tannin. The respective natural orders comprising the Dicotyledons vary greatly, as has been pointed out by Dr. Dekker, in respect to the manner in which tannin is distributed among the various families. In every order it frequently occurs that of two closely related families the plants of one will be rich in tannin while in the plants of the other, tannin will occur either in very small quantities or not at all. Occasionally there seems to be a gradual variation in tannin content between closely related families. Some natural orders contain no families of plants at present known to produce tannin, and in other orders almost the entire range of families furnish plants containing tannin but in very limited quantities. From the information which is at present available it does not seem possible to establish any very direct correlation between the production of tannin by different families of plants and their relationship to any of the schemes of classification which are in use by modern botanists. Since, however, most of the known facts concerning the distribution and abundance of plants have been collected and arranged with reference to the botanical classification it will be desirable to recognize

the usual divisions into orders and families for the purpose of more clearly setting forth the general facts concerning the geographical distribution of plants producing tannin.

Turning now to the actual question of geographical distribution of plants producing tannin, we may at once dismiss from consideration all of those families in the previously mentioned classification other than the seed-plants. We will consider for convenience of discussion each of the three main groups of seed-plants, beginning with the Gymnosperms. In this subdivision practically all of the plants known to contain tannin occur in one of four natural orders, the chief of which is the Pinaceæ, to which belong the pines, spruces, hemlocks and firs. The distribution of this group in the northern hemisphere naturally follows closely that of the coniferous forests and aside from the occurrence of a species of *Podocarpus,* in Southern Africa, and a species of *Phyllocladus* in Tasmania and New Zealand, there are no important tannin-bearing representatives of the Gymnosperms to be found south of the Equator. The distribution in the Northern Hemisphere coincides in a more or less general way with the principal mountain ranges, the slopes of which are naturally wooded with forests of coniferous trees. This of course tells nothing of the distribution in detail but merely indicates the densest areas on which plants of this group, having a high tannin content, may be found. Scattered generally throughout certain sections of the United States and Mexico, as well as through regions in Central and Northern Europe and Asia, are many tannin-bearing species which belong to this group, but since by far the largest number of important species are included among either the pines, hemlocks or spruces, it follows that the general distribution of this group of tannin plants conforms quite closely to that of these species of trees. So far as known it appears that the tannin-bearing Gymnosperms are practically confined to the north temperate zone, and because of their accessibility and the inroads made upon them in order to meet the increasing demands for timber it is probable that this source of tannin will be one of the first to be exhausted.

The second group of seed-plants, the Monocotyledons, is quite unimportant from the standpoint of tannin, although it contains many hundreds of species of plants which are well known and

widely distributed. Here, as was stated, belong the grasses, of which there are more than 3,500 varieties, but only four or five of these are known to contain tannin. In the one order which contains all of the tannin plants of importance, two only are worthy of mention here. These are the palmetto of Florida and *Areca catechu* of India, which is one of the commercial sources of cutch. There are 35 other orders in this group, the plants of which are widely distributed, but they are so poor in tannin that from the commercial standpoint at least they cannot be regarded strictly as tannin plants.

The third group of seed-plants, the Dicotyledons, contains by far the greater number of tannin plants. In some of the natural orders of this division tannin producing families are practically wanting, in some the relative number of tannin families is variable, and in others practically every family contains tannin producing plants. A study of those natural orders in which only a part of the families contain plants rich in tannin reveals some interesting facts. Several of these orders are widely distributed both with respect to climatic conditions and continental location. Representative species which contain tannin occur in various situations ranging from the tropics to areas approaching the limits of vegetation toward the poles. However, when the locality is considered, of such plants as have been found to yield tannin in percentages sufficient to make them commercially promising, it becomes evident that with few exceptions they are all to be found in tropical countries. This fact may be concretely illustrated by citing the distribution of some of the more important tannin plants belonging to those natural orders in which there is great variation between families with respect to tannin production. For example, the natural order Urticales has three tannin producing families comprising about sixty species of plants of which those highest in tannin, 4 to 14 per cent., are a few species of *Ficus* growing in India and the Philippines. In the order Santalales four families together contain about fifteen species of plants which produce tannin, the important ones being species of *Osyris* and *Fusanus* from India, Central Africa and Australia, ranging from 15 to 25 per cent. in tannin content. The order Ranales has nine families which together include a hundred species of plants containing more or less tannin; of

these the best known are species of *Persea* in Chili, 17 per cent. tannin; *Nectandra* in Brazil, 10 per cent. tannin; *Nesodaphne* in Australia and *Litsea* in India, both yielding over 7 per cent. tannin. In the order Tubifloræ a large number of tannin containing species is distributed among fourteen families. The important tannin plants are species of *Bignonia* from Guiana, 14 per cent. tannin, of *Eremophila* from Australia and of *Avicennia* from the East and the West Indies. Other orders in which a part of the families have numerous species containing tannin, the important ones of which are largely confined to the tropics, are the Contortæ Aristolochiales, Rubiales, Umbelliflora, Parietales and Malvales.

No less interesting is the distribution of those orders in which practically all the families comprise tannin bearing plants. In some of these families the occurrence of tannin is so general that they may be considered as typical tannin families. Examples of such are the Combretaceæ, consisting of about 240 tropical species, one of which yields the myrobalans of commerce; the Rhizophoraceæ which contains about 50 tropical species rich in tannin, some of which yield the mangrove bark; the Leguminosæ with about 6,000 widely distributed species of which many of those rich in tannin, as the wattle, algarobilla, ratanhia, kino and divi-divi, are tropical, and the Myrtaceæ which has at least 100 tannin species, the best known of which is the Eucalyptus, native of Australia. Notwithstanding the wide distribution of these families, by far the greater number of species having a high tannin content occur in tropical or subtropical regions. There are, of course, some exceptions, as, for example, the Fagaceæ, to which the oaks and chestnuts belong, but in general that portion of the several continents lying between the parallels of 30° north and south latitude must be depended upon to furnish the bulk of the supply of commercial tannin.

An enumeration of the various plants which have been used for tanning in different countries would give only an apparent indication of their geographic distribution since a tannin plant frequently occurs in countries where it finds little if any use and perhaps more frequently its greatest use is in countries where it does not naturally occur. In many cases it is equally unsafe to judge of the botanical distribution of these plants from the

localities given as the source of the material used in the analyses reported in the literature of the tannins. The writer recently examined what purported to be a list of the most important tannin plants of the world in which the country where each species occurred was given. On tabulating this list the following distribution of the species was obtained:

India	68 species	Chili	3 species
Europe	40 "	Brazil	3 "
Australia	22 "	Argentine	3 "
North America	16 "	New Zealand	3 "
Africa	9 "	Peru	2 "
Central America	7 "	Guiana	2 "
China	3 "	Asia	2 "
Japan	3 "	Mexico	1 "

A number of reasons might be given for the apparent inequality in distribution shown by this compilation but it will suffice to say that botanical exploration, particularly with respect to economic plants, has been carried much further in India and Australia than in other tropical countries, and that when these countries shall have been fully explored substantial additions will probably be made to their lists of tannin plants. In this connection mention may be made of a note by the writer in the JOURNAL of this Association[1] in which attention is called to thirty-five species of tannin plants in Paraguay, only one of which is referred to Paraguay in most of the literature on tannins.

The present state of knowledge with respect to the distribution of tannin plants leaves much to be desired. The lack of information is not confined to the conditions in the less accessible tropical countries alone, but is evident also wherever it becomes desirable to secure full details concerning the production, handling and utilization of any tannin plant. In the judgment of the writer there is less need for concern regarding the possible exhaustion of the natural supply of tanning materials than for a practical solution of the problem of how to bring them into the market on terms that do not work a hardship either to producer or to consumer. So long as these materials can be obtained from untilled or untillable areas of land with the assistance of low priced labor their production as an agricultural crop will prob-

[1] Stockberger, W. W., Tannin Plants of Paraguay, *Journal of the American Leather Chemists Association*, April 1912, p. 185-192.

ably be very limited. But should economic conditions so change as to enable certain tannin plants to compete successfully with general field crops there is no doubt that large quantities of tanning materials could then be produced on an agricultural basis. It follows, then, that the practical importance of a thorough study of the geographic distribution of tannin plants is twofold, first, since it will yield more definite information concerning the location and available quantity of existing tannin materials, and second, since it alone can furnish a rational basis for extensive experiments having as their aim the introduction of tannin plants into our present system of agriculture.

Dr. Stockberger showed a chart on which the distribution of tannin-yielding conifers was outlined. Mr. Yocum remarked that the areas on the Pacific coast covered by coniferous trees yielding tannin, although inferior to the hemlock, extended all the way from the Aleutian Islands to San Francisco. He also noted that no mention was made in the paper of chestnut and oak woods as sources of tannin.

Mr. Wallin asked whether canaigre could be grown at a profit. Dr. Stockberger replied that it could, if a market for it were assured. In this respect canaigre is an exception, tannin plants generally being not profitable to cultivate.

NOTE ON THE ANALYSIS OF TANNINS, II.

By Louis E. Levi and Aug. C. Orthmann.

In a former article (this JOURNAL, Oct., 1911, page 465) we gave the results of comparative analyses of extracts with our new method using reagent No. 33 and the hide powder method. The probable formula for reagent No. 33 is

$$Cr_2(SO_4)(C_2H_3O_2)_2CrO_4.$$

The analyses were all made after the removal of the insolubles. The following analyses show the results obtained with the above reagent on leached barks, etc.

TABLE I.

ANALYSIS OF BARKS AND NUTS, ETC., LEACHED AT TEMPERATURES GIVEN BY PROCTER.

Description	Per cent. Tannin by Hide Powder	Per cent. Tannin by New method
Mangrove Bark, Africa	38.44	39.42
Mimosa Bark, Australia	30.01	30.71
Quebracho Wood, Argentine	18.79	19.02
Algarobilla Pods, Chili	45.40	37.15
Algarobilla Pods, Chili	41.05	31.08
Myrobalans	29.36	28.01
Valonia	24.58	22.42
Oak Bark, Germany	11.28	8.72
Canaigre, Texas	18.65	21.90
Molle Bark, Argentine Republic	14.10	13.51
Mexico Bark, (Lysiloma Candida)	24.37	24.82
Oak Bark, California	11.40	13.89
Mallet Bark	45.76	31.43

The following qualitative tests show that the reagent does not precipitate the non-tannins after detannization with hide powder.

TABLE II.

QUALITATIVE REACTIONS OF NON-TANNINS FROM HIDE POWDER METHOD WITH:

	Reagent No. 33	Gelatine	K CN
Rove, Smyrna	No precipitate	No precipitate	Showed gallic acid
Sumac	"	"	"
Gall nuts	"	"	"
Quebracho extract[1]	"	"	"
Chestnut oak extract[1]	"	"	"
Canaigre	"	"	"

These non-tannin solutions were allowed to stand 16 hours with reagent No. 33 and showed no precipitate.

Aside from the fact that the reagent does not precipitate non-tannins (gallic acid) a most interesting point was discovered, namely: The above reagent does not precipitate the sulphite cellulose extracts such as Muskegon and Spruce.

We are now investigating this lack of reaction and will make it the subject of our next article and if the reagent proves to be all claimed for it, which is shown in the qualitative tests, we hope to have a method by which the chemist can determine accurately the amount of the actual tannins in tanning extracts or liquors.

[1] To each of these extracts was added 10 per cent. of gallic acid before detannization. After standing 16 hours at room temperature these two solutions were boiled and allowed to stand 24 hours longer, no precipitate formed.

The sulphite cellulose or other non-reacting substances are shown by the difference between the amount of tannin claimed and the amount found by use of reagent No. 33.

In the above and former (*J. A. L. C. A.*, Oct., 1911, page 476) preliminary analyses of extracts, barks, nuts, etc., the high results of the hide powder method are probably due to the absorption of the gallic acid by the hide powder and in our opinion the reagent No. 33 method represents more accurately the actual tannin contained. All these comparative investigations are to be continued and we hope in a future article to give the chemist a full and exhaustive résumé of our work with extracts, barks, nuts, leaves, etc., which have come to our notice.

It has also been observed that the addition of sulphite cellulose extract to tanning extracts increases the amount of insolubles. This will also be thoroughly tested and will be the subject of a future paper.

DECEMBER, 1912.

LABORATORY OF PFISTER & VOGEL LEATHER CO.

THE ROLE OF HYPO-SULPHITES IN THE LEATHER INDUSTRY.[1]

By Alfred Seymour-Jones.

At the recent London congress of the International Association of Leather Trades Chemists, Prof. Dr. Meunier read a paper demonstrating the results of his experiments with potassium carbonate and thiosulphates as dehydrating agents. The President, Dr. Gordon Parker and Prof. Procter referred in guarded terms to work which I had carried out during the past twenty years on the same topic and of which I had informed them and others privately. As Prof. Meunier has rediscovered certain phases of my work and thus given the lead for others to carry on similar investigations, I said at the conference that as "the cat was out of the bag" I would publish the results I have obtained and put into commercial practice with success.

This rediscovery of Prof. Meunier's at once brought to my mind the prophetic words by Prof. Procter in the introduction to

[1] From *Collegium* 1912, No. 511, p. 620.

his work, "The Leather Industries Laboratory Book," page XVII.—"In one way, indeed, chemistry must be admittedly unwelcome to the conservative Tanner—it is the key to mysteries believed safely locked within the doors of his factory! But, even so, it must be reckoned with, for, like the genii of the stories, it can neither be killed nor bound, but is fortunately the willing servant of all who have the intelligence to use it; and as capable of discovering new secrets as of throwing open the old ones." I congratulate Prof. Meunier upon his work and rediscovery, which causes me to publish the following statement. I do not propose to write out the details of each individual process but to indicate the results which may be obtained, and which I have secured in every day practice in the leather industry leaving it to the reader to apply the knowledge as he may.

Prof. Meunier enunciated a sound axiom, when he said, that "dehydration of the pelt is a primary and underlying principle in the production of leather." For this purpose sodium thiosulphate acts in a manner as yet not fully appreciated by the trade. For convenience of expression, I shall herein use the generic and trade term "hypo" to express sodium hyposulphite, or more strictly thiosulphate. Provided the hypo is ground fairly fine, it may be used favorably as a means of curing hides and skins. If prepared pelt is saturated with hypo and then treated to a weak acid bath, the result is a beautiful white leather dependent partially on dehydration, and partly on the deposition of sulphur. This leather, may be fatliquored and dyed, or stuffed with heavier fats or greases, and with suitable oils a species of chamois leather may be made. Instead of employing an acid, alum may be added to the requisite amount, which will react with the hypo and at the same time increase the tannage; or as I discovered about two years previous to the Pullman-Payne patent, an excellent buff leather can be made by the addition of formaldehyde. A similar leather may be made by using sodium acetate instead of hypo. If the hypo-leather is found to be too dry, salt, glycerine, or magnesium sulphate, etc., may be added to attract moisture.

In 1894 I discovered that alum would decompose potassium bichromate equally with acid, and applied it to the process of

chrome tanning for certain purposes. The addition of formaldehyde aided in reducing the stretching qualities of chrome leather. For many purposes, hypo acts as a desirable deliming agent and this feature should be studied by the tanner. One of the most interesting and as yet unexplainable uses to which hypo can with advantage be put, is, to remove grease and fat from pelt or leather. If greasy hides or skins are delimed with saturated hypo solution, or the skins after hypoing treated to a bath of acid, or the already cleansed skins similarly treated, or the skins first slightly swollen with acid and then given a saturated bath of hypo; in each case either in a paddle or drum, and are then subsequently worked out over the beam, the grease may be expelled. Or if the hypo is given to very greasy skins in a drum with just enough water to dissolve the hypo, the skins being also wet, say as from the drench (bran), and the hypo drummed well in to the pelts and then decomposed with acid, such skins can be chromed without the grease appearing subsequently. In the case of greasy butts which have been rolled, they should be suspended in a 10 to 20 per cent. solution of hypo in water of about 140 degrees F. for a few hours, when the grease will be found floating on the top of the liquor and should be skimmed off before taking out the butts. If the degreased butts are treated to acid after hypoing, then the leather will be materially improved in color.

As a bleach for dark colored leather, especially in the case of leather which has been overtanned and cracks easily, and is a bad color, the leather should be suspended in the same strength of hypo for 24 hours and then given a bath of weak acid. Such leather will be considerably improved in color and may be retanned or employed as dressing leather.

Hypo may be advantageously employed as a deleathering agent, which is best accomplished by drumming in warm water and hypo in dilute solutions, running away the waters as they become foul.

In 1892, I first employed hypo as a depickling agent of pickled pelts. This it does most efficaciously and without risk of injury to the pelt. To do this properly, it is preferable to perform the operation in a paddle, using about four-fifths of a pound of

hypo to the dozen. The acid will be rapidly and safely removed, and the skins can with advantage be washed and scudded afterwards.

In 1893 having some bad colored extract of quebracho in the factory, I succeeded in making an excellently bleached extract by means which have since been the subject of a patent. The result of this bleached extract in tanning attracted my attention to the use of hypo as a dehydrating agent prior to tanning. Experiments were carried out, with remarkable success. I found that if hides were treated with from 2½ per cent. to 10 per cent. of hypo either as a preliminary delimer or otherwise, either in a drum or paddle, and then submitted to neat extract, either in a drum or paddle or pit, the period of tanning was reduced in the case of the drum to a few hours and in the other instances to a few days, with corresponding excellence of color and weights which were phenomenal, and the leather so made commanded a ready sale. This system, I developed and have worked for years. The advantages apart from the rapidity of tanning, lay in the fact,. that experience taught one that the amount of extract necessary to produce a given weight of leather on given hides could be calculated to an exactness which bears no comparison with other processes. In average tanneries, the loss of tannin, is, I am informed, about 25 per cent. Those tanners who desire to save tannin in tanning sheep leathers will find it to their advantage to give the prepared skins a bath of about 10 per cent. hypo and add the tan direct. By this means, I have succeeded in producing excellent results with 1 pound of extract to the dozen. The method as suggested by me has been in operation in many yards on the Continent. In "The Tanner's Year Book" for 1907 page 135, I was amused to read a short article by Mr. C. E. Parker who outlined the principle I had been practising for years. The article is entitled "A New Principle in Tanning." The directions in which hypo may be utilized with advantage in the leather industry are so numerous, that it is impossible to enumerate all of them. I have for 35 years kept close records of all my experiments and have many such referring to hypo.

Incidentally, I may mention other leather-formers which should

receive the attention of tanners' chemists. Nearly all the sulphate salts are useful. A respectable white leather may be made by permanganate of potassium or sodium. The crude Ammonium sulphate from gas producer plants will make a satisfactory leather, the fixation being probably due to the presence of phenols. If pure ammonium sulphate is taken, the result is not completely satisfactory until phenol is added. Lead acetate is a useful salt for weighting chrome leather by precipitation. Practically all the mineral salts are leather formers by precipitation.

I have referred to decomposing by means of acid in the foregoing. For preference, I take in all cases an organic acid, principally formic, although lactic, acetic, butyric, etc., will also decompose the hypo.

DISCUSSION OF REPORT ON OILS AND FATS.

After the reading of the report on oils and fats (published in the December, 1912, JOURNAL) by the chairman, C. R. Oberfell, President Veitch called for discussion. L. Balderston offered some data in regard to the Dudley pipette (see page 47). T. Blackadder recommended the Ostwald viscosimeter, which he described. (See abstract, with cut, page 49.) L. Balderston expressed the opinion that the Gurney viscosimeter, (See JOURNAL, Vol. VII, p. 227), is preferable to the Ostwald instrument because it is more easily cleaned, stating in reply to questions from C. R. Oberfell that it may be easily calibrated, and that tubes of different sizes may be used for different oils.

Mr. Oberfell read part of a letter from a firm manufacturing sulphonated oils describing a method of determining percentage of water which does not include other volatile constituents. The method depends upon the contraction in volume of the oil when shaken out with acid and saturated salt solution. In answer to a question, Mr. Oberfell said that the methods tried by the committee gave concordant results for water and volatile matter, but that if these were to be separated some other method must be found.

J. S. Rogers suggested that the calcium carbide method might be employed; (see JOURNAL, Vol. VII, p. 630).

C. W. Norris remarked that with many oils slow drying methods for moisture give misleading results because they not

only lose volatile matter by evaporation, but gain in weight by oxidation. He then described the Marcusson method. A quantity of the oil is placed in an Erlemeyer flask with 50 to 100 cc. of xylol. The mixture is then distilled, and the distillate collected in a graduated tube. The water and xylol separate, the latter holding all the volatile matters other than water, and the volume of the water may then be read off directly.

F. H. Small described a method of testing emulsification value of oils. The desired amounts of oil and water are put in a 100 cc. Nessler tube, which is then put into the rotating shaker at a certain distance from the axis and the shaker run a definite time at a definite speed. By this method good duplicate results may be obtained.

C. R. Oberfell had tried the same method, but could not get satisfactory end-points.

Mr. Small used for an end-point the instant when a layer of water formed covering the bottom of the tube, and was able to duplicate results within a very few seconds.

C. C. Smoot, III., remarked that the evaporation test for mineral oils is misleading. An oil may show high evaporation loss, and yet in practice lose no more than another whose evaporation loss in the laboratory is low.

Mr. Veitch suggested that by fractional distillation it might be possible to get a correct estimate of water and also obtain an idea of the composition of the oil.

T. A. Faust asked about total fat determination. Mr. Oberfell replied that the difference between the sum of the percentages of water and volatile matter and unsaponifiable matter and 100 per cent. is taken as total fatty matter.

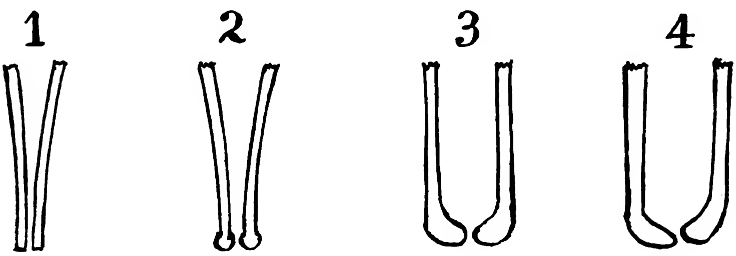
NOTE ON THE DUDLEY PIPETTE.

By L. Balderston.

The Dudley pipette as commonly used is similar in form to an ordinary pipette, holding 100 cc. between two marks, one just above and the other just below the bulb, and having an opening of such size that 100 cc. of water at 100 degrees F. will run out in exactly 34 seconds. If the temperature is 20 degrees C., the time is about 35 seconds. From Mr. Oberfell's report on fats

and oils in the last number of the JOURNAL, it is apparent that the Dudley pipette is not a dependable instrument for determining the viscosity of oils.

On examining his figures, I noticed that there is a rough proportionality among them. The observer whose results on one oil are highest gets highest on all, and the lowest results are also all by the same observer. All the pipettes gave the same reading for water at 20° C., but it occurred to me that small differences in the shape in the orifice would make a much greater difference to the viscous oil than to the water. It is impossible to make pipettes whose shape is exactly the same. In order to test the matter, I made a number of Dudley pipettes out of broken-tipped 100 cc. pipettes, having a mark above and one below the bulb, with a capacity of 100 cc. between the marks, correct to within 0.1 cc. I was fortunate enough to get four out of the lot whose time for water at 20° C. was between 32 and 39 seconds, and these four were used in the tests. The



shapes of the four tips are shown approximately in the cut. The results given are times in seconds.

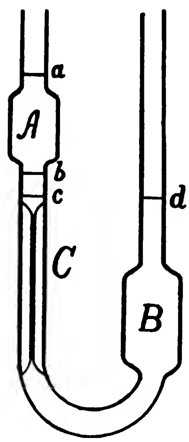
	Time for water at 20° C.			Time for oil			
Pipette	1	2	Average	1	2	3	Average
No. 1	32	32.5	32.25	164	163	166	164.3
No. 2	33	33	33	95	95	—	95
No. 3	33	33	33	90	92	—	91
No. 4	39	39	39	98	—	—	98

Numbers 1 and 2 look very much alike, but 1 is cut square off, and 2 has a fire-polished tip, and the fact that most of the taper of 2 is wider, prevented the oil from being so much hindered as in 1. The irregular form of aperture in 4 caused cross currents which hindered the rapid flow of the water, while the

slower flow of the oil was not hindered more than in the regular shaped orifice of the same size in 3. Oils of higher viscosity show a great difference between 2 and 3, the narrower taper of 2 offering more resistance to the heavier oil, and making it take more time than 3. It must be apparent that we cannot expect reliable results from the Dudley pipette. The Engler viscosimeter is much more reliable, the shape of the orifice as well as its size being perfectly definite. The cost is considerable, and the time required for each determination rather long. In both of these particulars the Gurney instrument, described in an abstract published on page 227, April, 1912, JOURNAL, seems to me to offer decided advantages. Mr. Cuthbert and I have done some work with this instrument, and hope soon to publish some results, with a picture of the apparatus and description of the method of calibration.

ABSTRACTS.

The Viscosity of Lubricating Oils. A. E. DUNSTAN and J. F. STREVENS. *J. S. C. I.*, XXXI, 1063-4. The authors believe that the viscosity of a lubricating oil can only be satisfactorily dealt with in the form of a temperature curve, so that the behavior of the oil can be predicted if the



working conditions are known. They hold that all measurements should be in terms of absolute viscosity, and recommend the Ostwald instrument. Oil is run in to the marks *c*, *d*. The instrument is now suspended in a bath of paraffin wax or clear high-flash oil, in which a delicate ther-

mometer is immersed. After the apparatus has stood at constant temperature for 15 minutes, the level is accurately adjusted to the level *cd* by means of a warmed pipette. A rubber tube is now attached above *a* and the oil sucked up above the mark *a*. It is then allowed to flow down, and the time of flow between *a* and *b* taken. Several readings are taken, and averaged. For ordinary oils the following dimensions are satisfactory: Capillary *C*, 6 cm. long, 1 mm. bore; bulb *A*, 4 cc., bulb *B*, 8 cc.; length over all, 15 cm. A series of readings between 70° C. and 200° C. having been made, a curve may be plotted, showing the variation of viscosity with temperature. The instrument is calibrated by means of a standard liquid whose viscosity is known. Pure phenol is very suitable for this purpose, and its viscosity at various temperatures is given. At 25° C., 0.0850; at 45°, 0.0404; at 50°, 0.0337; at 60°, 0.0253, and at 70°, 0.0197. If the flow of phenol at 25° in the given viscosimeter takes t seconds, we shall have $0.085 = Ktd$, where K is the constant of the instrument and d the density of phenol. From this equation K is found. The viscosity of any other substance is then found by multiplying the value of K by the time in seconds, and by the density of the substance. A chart shows curves for several oils.

Dyeing of Chrome Leather. JOSEF L. NEJELDY. *Allgemeine Gerber-Zeitung*, Nov. 30, 1912, No. 48, p. 3. Chrome leather behaves differently from bark leather in the dyeing process. The dyer must be careful to see that any free acid developed during chrome tannage is neutralized, or it may influence the color, and may also release fatty acids from the soap used in fat-liquoring. The neutralization is done with borax, sodium phosphate or bicarbonate in a lukewarm bath, and is followed by a warm rinse. Four kinds of dyes are used: basic dyes, acid dyes, "substantive" or direct dyes and alizarin dyes. The last two are especially suitable, but alizarin dyes are too expensive to be generally used. They are employed for light shades such as straw, and where colors fast to light are necessary, or for dyeing clear through. "Substantive" dyes are chiefly used for chrome leather. They have the advantage of coloring the leather directly in the color-bath, and make possible a deep, full color. The color-base which unites with the chrome salt to form a water-insoluble lake, unites with the chrome-hide compound and gives a color fast to light and inactive toward alkaline fat-liquors. These colors may be mixed with vegetable tanning materials or logwood to form one-bath dyeing liquors. A full and vivid color may be given to chrome leather by a bath of sumac extract and a substantive dye (the tannin being fixed by tartar emetic), followed by a second bath of a basic dye. All the commercial blacks for chrome leather belong to this group. A 1 per cent. logwood bath gives a deep black on the grain, but dark violet on the flesh side. Noteworthy dyes of this group are: For yellow, pyramine yellow, pyramine orange, oxamine brown, G, 3G, GR, R; for red, cotton red 4B, oxamine red 3B; for blue, oxamine blue 3R, BG; for green, oxamine green G; for black, cotton black, chrome-leather black EA extra.

Many of these are as fast to light as the alizarin dyes. The acid dyes may be used for chrome leather, especially when it is desired to dye the leather through. These dyes also color the leather direct, but no free acid must be present in the bath as when these colors are used with bark leather. For light-fast dyeing the following process is recommended: The first bath is made of an acid dye and a vegetable dye, such as sumac or fustic. Before the color is put in, ½ per cent. of tartar emetic is put in the bath to fix the tannin on the fiber. The leather is well rinsed and placed in a second bath of basic dye, which gives depth and brilliancy to the color. The most used dye of this group is nigrosine. Different brands of nigrosine give different shades, some yellowish, some reddish and some bluish. Basic dyes are used but little for chrome leather, and mostly in conjunction with materials containing tannin, as sumac, gambier, etc. Chrome leather is fat-liquored after dyeing. Among the various fat-emulsions which consist mainly of neats-foot oil or castor oil and soap, to which may be added egg-yolk and moellon, the best suited for colored goods is sulphonated neats-foot oil. This is almost neutral, while the other mixtures always contain free alkali. The sulphonated oil is prepared by adding to the oil, a drop at a time, with vigorous stirring, 15 to 25 per cent. of its weight of concentrated sulphuric acid, the temperature not being allowed to exceed 40° C. The mixture is allowed to stand from 12 to 24 hours, and the excess acid is then washed out first with saturated salt solution and then with water. The oil dissolves easily in hot water, forming a good emulsion which is rapidly taken up by the leather. It is well to add to the water solution ¼ per cent. strong ammonia to neutralize the remainder of the free sulphuric acid. A suitable quantity of fat-liquor is 5 per cent. of the weight of the damp leather. Another process may be used for basic dyes. The skins after neutralization are treated with a 5 per cent. sumac bath, with ¼ per cent. tartar emetic, then fat-liquored and dried. They are then sorted into various shades, dampened with hot water in a paddle wheel and then dyed with a basic dye. By this method the loss of dye in the fat-liquoring process is avoided. This method gives very good results in the making of "elk" leather as it is done in America. L. B.

The Acidity and Alkalinity of Natural Waters. JAMES WALKER and T. A. KAY. *J. S. C. I.*, XXXI, 1013-16. Indicators are commonly used, but not only do different indicators give different results, but the same water will often be classed as alkaline by one analyst and acid by another. The electrometric method is accurate and reliable, but troublesome to use. The authors' method involves comparison of the water to be tested with standard solutions whose acidity or alkalinity is known. Pure water has chemically equivalent amounts of hydrogen ions and hydroxyl ions. The normality of water and of any really neutral solution in terms of hydrogen ions varies rapidly with change of temperature. Values given by A. A. Noyes are as follows: 0° C., 0.30×10^{-7} (that is, 0.00000003 normal); 18° C., 0.68×10^{-7}; 25° C., 0.91×10^{-7}; 100° C., 6.9×10^{-7}

This method of stating acidity or alkalinity is not suited for practical purposes, because of the rapid variation with temperature. The authors therefore propose to state acidity and alkalinity in terms of that of pure water at the same temperature. Water is taken as a standard substance in estimating specific gravity, specific heat, etc., and the authors propose to use it as a standard for acidity also. Thus a water whose acidity at 18° C. is 1.36×10^{-7} has a relative acidity of 2, and a relative alkalinity of ½.

The standard solutions are made from disodium hydrogen phosphate and monopotassium dihydrogen phosphate. A mixture of 11 parts of a solution containing 23.88 g. of $Na_2HPO_4.12H_2O$ per liter, with 989 parts of a solution of KH_2PO_4, 9.08 g. per liter, has a relative acidity of 100. A mixture of 612 parts of the former with 388 of the latter is neutral. A table is given showing the relative acidity or alkalinity of fifty mixtures. Two modes of procedure are described. The first applies to colorless samples or those which will settle clear on standing. Filtration must be avoided, as the acidity is almost certain to be altered. Twenty-five cc. each of the water to be examined and of the neutral standard are measured into two porcelain dishes of 150 cc. capacity, 1 cc. of a 0.1 per cent. solution of azolitmin added to each, and the tints compared. If the sample is decidedly acid, 25 cc. of the acid phosphate is measured into another dish, the indicator added, and alkaline phosphate solution run in until the tint matches that of the sample. The volume of the sample must be kept about equal to the mixture by adding more water and indicator, so that the depth of color as well as the tint may be comparable. If the sample is alkaline, 25 cc. of the alkaline phosphate is measured out, and acid phosphate run in until a match is obtained. Tables are given showing acidity and alkalinity corresponding to many different added volumes.

If the water sample is colored, the above method will not give accurate results. In such a case, a preliminary titration is made by the method already described and a second is then run, having placed the water sample with indicator in a glass tube so that the light which illuminates it passes through a tube of distilled water, and the phosphate standard in another tube so placed that the light illuminating it comes through a tube containing the water under examination without indicator, thus compensating for the natural color of the water. Samples should not be diluted, as the acidity will be changed.

The Dyeing of Chamois Leather. W. EITNER. *Gerber,* 1912 [38], 255-6, 269-71, 283-5, 297-9. This extended article appears in response to requests for a discussion of this process which often is unsatisfactory in outcome; the dyeing of suéde leather is also included since the process is the same. Chamois leather requires a more careful treatment in the preparation (Brochiren) since the excess of tanning agent (oil) is not removable by water and further it is necessary to bleach the yellow color peculiar to this tannage. This bleaching has from early times been effected by

exposure to the sunlight. This is repeatedly alternated with a washing with alkali which removes the oily products from the surface of the fibers. Neutral oil soaps like Marseille soap or genuine sulpho-oleate soaps from castor oil are best for this. Soda is sometimes used, but the leather is then apt to lose softness. The natural bleaching is preceded by working the leather with a solution of 2 parts soap in 100 parts water at 37° C., wringing out and rinsing; this removes the unfixed fatty substance. After a day's exposure to the sun, the washing is repeated with 1 per cent. soap and the next time with ½ per cent. and so on until desired effect is reached. After each wringing out the side to be dyed or curried white is worked with pumice.

Sun bleaching is the safest, least affecting the softness of the leather. As a substitute, the chemical methods used for wool are employed. The leather degreased as above is soaked in lukewarm water, then pressed or centrifuged and then brought into a cold weak solution of potassium permanganate. The leather is agitated in the bath (which is gradually strengthened as required), the degree of the reaction being marked by the browning of the leather and the liquor. The leather is then washed with cold water and treated in a second bath of sulphurous acid until the brown color is fully discharged. When more cautious treatment is desirable, the above bleaching is carried out with weaker solutions, the operations being repeated. Another chemical bleach is with hydrogen peroxide. After a soap wash the leather goes into a peroxide bath containing 20-25 per cent. of leather weight, at 35° C. Salammoniac is previously added to the peroxide, 5 per cent. of its weight and the whole is gradually added during the agitation of the leather. When bleached sufficiently, the leather is rinsed first in acidulated, then pure water.

The fells intended for white are spread flat upon a table and the following mixture applied with a brush: 20 parts oleate soap, 1 part dextrin are dissolved in 100 parts warm water and 40 parts castor or bone oil stirred in and further after cooling, 2 parts rice starch, ½ part lithopon. This application restores to the leather its original softness and clears its color. The above fat luster is generally diluted and applied twice.

For black chamois leather no bleaching is needed. The old-fashioned process still used by glovemakers was to coat the dry leather with the various mordants and dyestuffs. Such dyes are superficial and wear off. A more durable color is obtained by softening the leather, washing with soap, rinsing and pumicing, then mordanting. For this last, 3 k. chrome alum to every 100 k. leather are dissolved in 15 l. water and to this 300 g. calcined soda dissolved in water are added. This stock solution is diluted with 130 l. water and in this the leather is milled ½ hour, then drained and dried; this effects an after mineral tannage. After such a mordanting, the black may be dyed without fear of striking through. For the dye, 5 parts logwood and 50 parts water, 1 part fustic and 50 parts water, 1 part myrobalans and 10 parts water are separately boiled down to 40, 8 and 8 parts of liquor, then united and made alkaline with

0.1 part potash. Extracts are also used but often give inferior colors. Finally 0.02 part (200 gms.) potass. bichromate are added. The liquor is applied in two coats, adding one-ninth volume of iron liquor the second time; a third coat contains 4 parts iron liquor, 1 part dye liquor. The iron solution consists of 5 parts ferric alum, 2 parts titan. ammon. oxalate in 100 parts lukewarm water.

Towards the end of the currying, the leather receives a fat luster to intensify the black. One kilo of vaseline oil is mixed with a kilo of soft oleate soap or monopol soap may be substituted melted with half its weight of water. The whole is gradually diluted with 5 parts water, first hot, last luke warm. This luster does not grease the leather but only deepens its color. Glossing agents like gums, glue, etc., are wholly out of place here.

The latest methods used in chamois leather dyeing are those employed with suéde leather, generally dyeing in the tub while the brush process is used for body or for adjusting shades. Careful cleansing of the dye-tubs after use is essential, not only by rinsing, but rubbing with soda and sand; miscoloration of leather can often be traced to contact with old dyes retained by the wood. Vegetable dyes are used most but aniline dyes can be toned down in combination and are not always so fugitive as some assume. Those vegetable dyes are preferred which contain tan-stuffs. Direct tannins are also used and unlike glove leather from the alum tannage, the chamois leather being more perfectly tanned, does not shrink. Catechu, a genuine tan, gives a very fast brown with chrome mordant and is also used in a prepared form made by previous treatment with bichromate. Myrobalans which gives a blue black with iron salts is best extracted in the whole fruit, since the splinters from ground hulls might foul the plush of the leather and the oil of the kernel has an objectionable odor. Willow and alder are good for grays and brown, but are often replaced by myrobalans and mangrove. Mangrove is a cheap and efficient substitute for catechu. The real dyewoods which are used are logwood, Brazil wood and Cuban fustic. Their decoctions are let settle 2 days and require no filtration. Manufactured extracts from the same woods are more convenient and much used.

Before dyeing, the chamois leather is first thoroughly softened if not fresh from the bleach and for light colors is mordanted with 3 kg. alum for 100 kg. dry leather; the alum is dissolved in 50 l. water, made basic with 270 gms. chalk, finally decanted and diluted with 150 l. water. The leather is milled in this ½ hour at 50° C., drained and then transferred to the dye vats. For these liquors Cuban fustic is used for plain straw yellow, tempered with extr. weld for milder shades; bright shades are obtained by blending with an acid aniline dye such as Fast Yellow S, Fulling Yellow O, Cassella. Saffron sometimes used is not at all fast. Grays are produced by combining tanstuffs (myrobalans extr.) with iron salt and logwood with alum. salts. Exact tones are best obtained by finishing with the brush on the table; lithopon white is treated with the

same mordants and dyes as used with leather and used for coating. For browns the mordant consists of equal parts of white and chrome alums made basic. Catechu is the tannin base shaded with fustic, Brazil wood or logwood and darkened with bichromate or still more with copper sulphate. Titan. salts give fine tones, either added directly to the catechu or applied separately with the brush. For light shades catechu may be replaced by oak, pine or willow bark; alder with mangrove are especially suitable and the alder may be replaced by fustic. Red, blue, green, etc., formerly prepared from vegetable colors, are easiest obtained from aniline dyes. The leather is prepared in the same way, alum. acetate being the mordant, prepared by adding a solution of 1½ k. sugar lead in 5 l. water to 3 k. alum (for 100 k. dry leather) in 10 l. water. The decanted solution is made basic with 300 g. calcined soda. Ordinary alum mordant can also be used. Basic dyes have more body than the acid dyes; they are preceded by a grounding with myrobalans and fustic. The dye must be made acid with ¼ its weight of acetic acid mixed with an equal amount of water and finally used in 1 per cent. stock solution. For all tub dyeing 2½ parts liquor to 1 part dry leather is a suitable ratio.

In carrying out the dyeing process, the mordanted leather is drained but not wrung or pressed, since dry spots dye unevenly. The dyeing begins with a small amount of the dyestuff and constant agitation, the dye being replaced as consumed. The leather is removed from the bath while the dye is replenished, to avoid spotting. It is necessary to dye very gradually with chamois, and the labor is much reduced by using a dye apparatus consisting of a skeleton drum revolving in a trough which is fed with fresh dye from below through a perforated tube. The dyeing is generally finished by brushing on the table. Immediately after tub dyeing or brushing, the leather is washed without delay; if let lie, the colors come off and spots result. The leathers are next stretched on the table and hung up to dry. The old practice of oiling after dyeing is no longer followed being unnecessary if the degreasing was effected with neutral soap and likely to soil the leather. W. J. K.

Method for Distinguishing Tannin Extracts. R. LAUFFMANN. *Ledertechn. Rundschau,* 1912, 353-4. This method worked out in the Freiberg Versuchsanstalt depends upon the differential precipitation of tannins by a mixture of equal volumes of a 10 per cent. ammon. molybdate solution and a 15 per cent. ammon. chloride solution. The assay solution, containing approximately 4 gms. tans in 250 cc. is filtered and 10 cc. mixed with 10 cc. of the reagent and let stand for 2 hours. The liquid is then filtered off and 10 cc. evaporated to constant weight. The ppt. (which cannot be washed for drying) is dissolved in hot water, united with the remaining half of the filtrate together with rinsings and this solution is likewise evaporated to constant weight. The difference in weight between these two residues gives the weight of the ppt.

The non-tans are determined as usual by the filter method and the weight of ppt. computed corresponding to 100 parts of tans; this is called

the "molybdenum number" and for 3 untreated quebracho extracts was found to range from 28.7 to 37.3; for 10 treated quebracho extracts 5.0 to 36.9 (lowest values when most sulphited); 3 mangrove extracts (untreated) 124.2 to 144.5; 3 mangrove extracts (treated) 111.3 (much sulphite) to 127.5 (no sulphite); 1 mimosa extract 128.1; 4 chestnut extracts 195.3 to 224.3; 2 oak extracts 197.7 and 205.8; 2 myrobalans extracts 122.2 and 108.0; 1 sumach extract 132.8.

From this it is concluded that a quebracho extr. which has a Mo number above 30-40 and shows neither pyrogallol tans (Stiasny's formaldehyde reaction) nor cellulose extr. (Procter-Hirst reaction) may be classed as mixed with mangrove; for strongly sulphited liquors the lower number 30 is taken as limit. The Mo numbers for chestnut and oak are essentially higher than for mangrove and myrobalans; an addition of chestnut or myrobalans to quebracho would raise the number while myrobalans mixed with oak would lower it. Pyrogallol tans added to quebracho can be further confirmed by Stiasny's test. Cellulose extracts were tested; 5 gave no ppt. and 2 gave crystalline ppts., while the normal form is flocculent. A check test upon 2 prepared mixtures of 2 parts sulphited quebracho extr. with 1 part mangrove extr. gave numbers 55.0 (57.5 computed) and 48.9 (49.9 comp.).

Trials of this method are requested and the author intends to apply it to other combinations as well as to search for other reactions which may render characteristic "numbers." W. J. K.

An Interesting Correspondence Concerning the Results of Analysis of Tannin Extracts. *Ledertech. Rundschau*, 1912, 329-32, 337-8. Under this title is published the text of 12 letters exchanged between L. J. Levinstein & Sons, Berlin, and the Freiberg Versuchsanstalt. The above firm disputes the accuracy of the Institute analysis of a certain chestnut extract, 1.6 per cent. insoluble being reported, whereas the firm finds 0.6 per cent. At request, the Institute repeats the analysis, finding 1.1 per cent. the second time. Hereupon the firm has control analyses made by other chemists which substantially agree with their own. Dr. Paessler states that errors of 0.6 per cent. are allowable in such analysis; that in this particular determination involving two measurements (total solids and total solubles), the errors may be in opposite directions making a total discrepancy of 1.2 per cent. He suggests that the lower amounts found by the other analysts are due to failure to filter to absolute clarity, a rule stringently observed at the Institute. Further such a low content as 0.6 per cent. insolubles can be judged by inspection which in this case agreed with the higher results actually found. Dr. Paessler has the advantage of courtesy in this correspondence since he is accused directly of not repeating the analysis at all but of computing the figures to suit the situation! His final word is that it is evident that the intention of the firm is to arouse public distrust against the reliability of the methods of research. The analyses were:

	Freiberg (1)	Freiberg (2)	Levinstein & Son	Berlin Maschke	Berlin Jablonski	Drs. Hundeshagen & Philip (Stuttgart)
Tans	31.2	31.1	32.0	32.8	32.3	31.2
Non-tans	8.7	8.7	8.5	8.1	8.7	8.8
Insoluble	1.6	1.1	0.6	0.4	0.7	0.7
Water	58.5	59.1	58.9	58.7	58.3	59.3

W. J. K.

Decolorized and Clarified Extracts in the Tannery. Marius Armand. *Le Marche des Cuirs,* 1912 [24], 370-2. The relative value of these two forms of chestnut extract is of concern to those who do not object to the color or who bleach their leather. It is commonly assumed that decolorizing the extract removes some tannin and the unbleached extract brings a higher price. In the manufacture of the clarified extract the liquor from the diffusors is chilled to 25° and let settle 60-80 hours, then concentrated; for decolorized extracts, a considerable amount of blood is added to the cooled liquor which is afterward decanted and evaporated.

Analysis:

	Clarified ext.	Decolorized ext.
Absorbed by hide powder	29.0	29.2
Non-tans, soluble	11.0	11.6
Insoluble	1.3	0.1
Water	58.7	59.1

The author has tested the relative behaviors of these extracts in tanning the "cuirots" of Mazamet. These are sheepskins which have been sweated, de-wooled and dried (this Journal, 1909 (4), 242). The material is considered especially suited for such experiment. Sixty cuirots were subjected to uniform preparation and 30 each given parallel tannages of 8 days.

Weights in kilos:

	Cuirots trimmed	White pelt =	Dry hide	Extract	Dry leather	Leather yield dry hide = 1
Clarified Ext.	15.75	50.6	11.15	19.5	14.2	1.273
Decolorized Ext.	15.75	46.25	10.25	19.5	14.5	1.414

More precise results might be obtained by making N determinations but it was preferred to make the study strictly practical. It is seen that the decolorized extract gave the highest rendement. Consequently less extract should be required to give equal rendements as confirmed in a second series of experiments:

	Cuirots, trimmed	White pelt =	Dry hide	Extract	Dry leather	Leather yield dry hide = 1
Clarified Ext.	14.0	39.5	6.5	13.25	8.0	1.24
Decolorized Ext.	12.0	40.0	6.9	12.0	8.75	1.268

The author believes these results would equally apply to heavy hides and that the decolorizing process yields a purer, more concentrated tannin.

W. J. K.

Estimation of Fats in Leather with Trichlorethylene. E. Goldberg. *Ledertech. Rundschau,* 1912, 49-50. The author has tested with favorable results Neumann's process (used on fodders) for the extraction of fats without heat. Comparative extractions were made of 21 leathers by CS_2 in the Soxhlet apparatus and by cold trichlorethylene. The greatest difference was 0.5 per cent., the trichlorethylene generally giving the slightly higher values. The procedure recommended is to shake 10 gms. cut leather with 100 cc. solvent for 1 hour, filter and evaporate 50 cc. in an extraction flask to constant weight. W. J. K.

To Re-dye and Work Over Mis-dyed Skins or those Discolored by Storage. "M." *Gerber-Courier,* 1912 [53], No. 46. The usual resort is to cover with a new dye or give a mere superficial re-working. This is generally of no use, the fells becoming either worse or returning to the old state. More radical treatment is necessary. In the case of greased leathers, when the black has been attacked by the spewed fatty acids, it is sufficient to dissolve away the coating of acid with soda or potash solution and give a new grounding, blacking, etc., in the usual way, being careful to first wash away the soda. Dyed leathers are more difficult. Light hues can be dyed in darker shades after thorough milling, and dark colors can be over-dyed with black; it is useless to attempt to brighten the leather again. The fells are first dyed lilac on the flesh side with a mixture of red and blue or direct with methyl violet; then milled 2 hours in a logwood decoction with a little alum. They are then ready for dyeing with iron black, best after passing through a weak bath of chromate of potash.

Dyed leather sometimes reveals too weak color or mis-matched tones during currying. The fault may be remedied in gloss leather by cautiously adding dye to the water used for moistening before rolling. With shagreen, the dye may be added during the shagreening which insures equal distribution. Fine red and bright blue fells often show a white coating over the grain after storage. This comes from excessive use of sulphuric acid in dyeing and is irreparable. It can never happen if the sulphuric acid bath be kept to always taste of acetic acid and the bleached fells afterward thoroughly rinsed. W. J. K.

PATENTS.

Process of Treating Waste Sulphite Liquor. U. S. Patent No. 1,043,303. Walter H. Dickerson, Muskegon, Mich., assignor to Tanning Extract Co. of New York. The addition of sodium chloride to the liquor has the effect of gelatinizing it when concentrated.

Machine for Stretching Tawed and Chrome Tanned Hides and Skins. U. S. Patent No. 1,045,203. E. Simeon, Grenoble, France.

Apparatus for Baking or Curing Patent Leather. U. S. Patent No. 1,045,623. W. R. Smith, Buffalo, N. Y., assignor to Buffalo Leather Co.

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T. A. Flynn, % Perfection Oil Co., Olean, N. Y.

Frank J. Heap, 225 Purchase St., Boston, Mass.

Harry P. Gregory, % New York Tanning Extract Co., Greenpoint, Brooklyn, N. Y.

F. A. Loveland, 425 East Main St., Corry, Pa.

CHANGES OF ADDRESS.

Oma Carr, to 14 Wautauga St., Asheville, N. C.
Paul A. Esten, to 195 Walnut St., Stoughton, Mass.
Frank L. Howes, to 325 Summer St., Boston, Mass.
J. Edgar Rhoads, to Box 905, Wilmington, Del.
August H. Vogel, to P. O. Box 37, Milwaukee, Wis.
Herbert E. Cox, to % Northwestern Leather Co., Portville, N. Y.
A. H. Lockwood, to 154 W. Randolph St., Chicago, Ill.
W. T. Buchanan, to Westminster Hotel, Westminster, Md.
Harry M. Johnquest, to 299 High St., Newark, N. J.
V. H. Kadish, to 388½ Summit Ave., Milwaukee, Wis.

ELECTION OF MEMBER OF COUNCIL.

The ballots cast to dissolve the tie between L. Balderston and C. Eachus for member of Council were counted by R. W. Griffith and E. J. Haley, tellers appointed by the President of the Association, on January 2. The result, as certified by the tellers, was the election of L. Balderston.

BOUND VOLUMES OF THE JOURNAL.

Copies of Volume VII. of the JOURNAL, for 1912, are now ready, bound in cloth or half morocco. Volumes I, II, III, IV, V and VI in uniform binding, may also be obtained. Price $6 per volume, delivered. Bound volumes will be exchanged for complete sets of unbound numbers at the rate of $1.20 per volume delivered. Missing numbers will be supplied at 25 cents each. Unbound numbers for exchange should be well packed and sent to the Manager at Ridgway, Pa., expressage prepaid at the "printed matter" rate.

COUNCIL.

A meeting of the Council of the American Leather Chemists Association was held at the Grand Union Hotel, New York, on Saturday, January 4, 1913. Present: Messrs. Alsop, Reed, Norris, Small, Oberfell, Hoppenstedt and Balderston.

The Secretary was instructed to send out with membership

application blanks a slip calling for detailed information in regard to the applicant's training. In case of application for active membership unaccompanied by such information, the Secretary will send such a slip and hold the application pending its return.

Correspondence between ex-President Veitch and Dr. J. G. Parker with regard to the proposed Procter International Research Laboratory was read.

Professor Procter retires from the faculty of Leeds University next year because of the age limit. He has consented to give his services without compensation to direct the work of investigators who wish to study problems connected with leather chemistry and manufacture.

It is proposed to erect a building for the purpose on the grounds of the Leeds University, and to place the laboratory under the care of the University, and to raise $10,000 for the building and $40,000 for an endowment fund. The institution is intended to be international in its scope, providing facilities for research work which may be used by students from any part of the world. An international committee is being formed to perfect plans, secure funds, and push the work to completion. The President was authorized to appoint a committee of active and associate members who shall procure the fullest possible information, in order that the matter may be presented to the members of the American Association and the tanners of the United States as clearly and definitely as possible. This committee are to report to the Council. The International Association of Leather Trades Chemists has appropriated one hundred pounds in aid of the project

After some general discussion in regard to committee work, it was decided that the Council should appoint for each committee a nucleus to consist of three men, so selected if possible as to be able to get together. These three shall be responsible for the work of the committee, but all the members shall have opportunity to choose which committees they will join.

The question of standardizing laboratories was discussed. It was agreed that good might result from having a competent man visit laboratories which are doing commercial work and

bring them into harmony. The Council thought, however, that the expense of such a work should not be borne by this Association, but rather by the tanners and extract makers.

The proposed new method of analysis of vegetable materials containing tannin was discussed. (This was printed in the JOURNAL for June, 1912, pp. 294-300.) The Council voted to approve the recommendations of the committee, and submit them to a vote of the Association in accordance with the by-laws. A number of suggestions in regard to changes in details of the method having been made, the President was instructed to appoint a committee to consider these and report their judgment.

The President was instructed to appoint a committee to propose a revision of the published provisional methods of oil analysis.

The Council then proceeded to choose committees as follows:—

Purification of Tannery Wastes: F. P. Veitch, Chairman; F. A. Loveland, C. M. Morrison.

Oils and Fats: C. R. Oberfell, Chairman; C. W. Norris, T. A. Faust.

Sulphides in Lime Liquors: Douglas McCandlish, Chairman; Louis E. Levi, J. V. R. Evans.

Proper Sampling of Leather for Analysis: F. M. Loveland, Chairman; Thomas J. Mosser, C. C. Smoot, III.

Analysis of Lactic Acid: H. C. Reed, Chairman; the other members to be selected by the Chairman.

Salt Stains: John H. Yocum, Chairman; James A. Connelly, C. M. Morrison.

Comparative Analysis: C. R. Delaney, Chairman. When the committee on further revision of the method of tannin analysis shall have completed their work, the chairman of this committee shall send out samples to test the value of any proposed changes.

The Question of Sampling: C. W. Norris, Chairman; T. A. Faust, H. C. Reed, E. J. Haley.

Sulphite-cellulose extract. This matter was discussed at length. The council approved the action of last year's committee in confining its work to the matter of the analysis of sulphite-cellulose extract, avoiding any question in regard to its commercial usability. The amendment proposed by Mr. Yocum at

the annual meeting (see p. 87 this issue), was rejected. The recommendation at the close of the committee report presented at the annual meeting (see p. 79 this issue), was rejected. The Council then adopted a recommendation that when materials containing sulphite-cellulose extract are analyzed, the fact shall be noted on the report that the material contains sulphite-cellulose extract. A committee to continue work on this subject, particularly to make further tests of the delicacy of the Procter-Hirst aniline reaction; F. H. Small, Chairman; H. C. Reed, L. Balderston.

Acidity of Liquors. No committee appointed. The Secretary was requested to announce that individual work in this subject is recommended.

Leather Analysis. The recommendations in Mr. Veitch's report were approved. (See report in the JOURNAL for December, 1912.)

Color Testing: William P. Maxwell, Chairman; L. M. Richeson, F. H. Small.

Estimation of Free Sulphuric Acid in Leather: F. P. Veitch, Chairman; L. A. Cuthbert, C. C. Smoot, III.

Determination and Estimation of Tanning Materials in Admixture. No committee. Individual work to be asked for.

REPORT OF THE COMMITTEE ON THE "ANALYSIS AND DETECTION" OF SULPHITE-CELLULOSE EXTRACT.[1]

By F. H. Small, Chairman.

The Council of the A. L. C. A. at its meeting December 3, 1910, appointed the writer of this report Chairman of a Committee to investigate the subject of the *"Analysis and Detection"* of Sulphite-Cellulose Extracts. His Committee was expected to report at the annual meeting held in December, 1911, but so little was accomplished by the Committee that no report was presented. Despite this poor showing the Committee was continued by the following Council and the Chairman reappointed. As is the present custom, members of the Association who were

[1]Read at the Ninth Annual Convention of the *A. L. C. A.*, Washington, D. C., December 6, 1912.

interested in the subject assigned the Committee were asked to notify the Chairman of their willingness to participate in the work and in this way a committee of some half dozen members was formed. Work was done and results submitted by Messrs. Reed and Veitch. They have been over this report with the Chairman and endorse it as submitted. In addition to the results of Messrs. Reed and Veitch other data will be found in the report which the Chairman has secured by correspondence or otherwise.

While it has been difficult to secure active co-operation in the Committee work, this does not seem to have been the result of lack of interest, for the subject of sulphite-cellulose extracts has been a live one at the various conventions since 1909 and various articles relating to such extracts have appeared in the JOURNAL.

The original appointment of this Committee was the result of a discussion at the 1909 Convention in the course of which Mr. Haley said "When conditions arise that call for change either in the method" (of tannin analysis) "or in the method of reporting, it is up to the Association to embrace the opportunity and it strikes me that the time has now arrived when some active measures must be taken to protect the integrity of the Chemists' reports according to the Association's methods. We cannot—— say this" (referring to the material in sulphite-cellulose extracts which is absorbed by hide powder) "is not tannin when each and every one of you Chemists report it as tannin. You are either prevaricating in your reports or else your method does not cover this special material and other kindred materials I could mention." I quote this to show that it was the question of the *Analysis* of sulphite-cellulose extracts that was the burning one at that time;—and what was true then is equally true now. The Committee was appointed to investigate the *analysis* and *detection* of sulphite-cellulose extracts. The discussion in Council when the Committee was appointed was on the question of analysis and while no specific instructions were given the Chairman he understood that what was most desired was an opinion on the legitimacy of the analysis of sulphite-cellulose extracts by the official hide powder method of tannin analysis. Mr. Claflin presented a paper at the 1911 Convention on the "Tanning Properties of

Waste Sulphite-Cellulose Liquors," but the discussion which followed was on analysis. During the current year Mr. Loveland has published an article on the "Analysis of Sulphite-Cellulose Extracts" and Mr. Wisdom one under the title "What is Tannin?", this latter despite the title being practially an argument on the propriety of the analysis of sulphite-cellulose extracts by the official hide powder method.

I have given this brief resumé because I think it important to emphasize the fact that the interest of our Association in sulphite-cellulose extracts has centered about the question of analysis. This limitation of interest, the Committee believes to have been wise. The *commercial* usefulness of sulphite-cellulose extracts is rather a subject for investigation by the Research Department of the Tanners Institute, the individual tanners, or the manufacturers of the extracts. This would seem to be the case,—if for no other reason,—from the fact that the sulphite-cellulose extracts on the domestic market are really proprietary articles. Mr. Claflin in his address at the 1911 Convention remarked in reference to sulphite-cellulose extracts, "It seems to be a question of how the waste liquors are treated and how much purified and if sufficiently purified and properly treated, there is to my mind little doubt but that the tanning properties of these liquors will be found to be far greater than the most sanguine of us now anticipate." That the usefulness of sulphite-cellulose extracts for tanning is dependent upon the mode of preparation is a fundamental article in the creed of the domestic manufacturers of sulphite-cellulose extracts. In other words, an investigation of sulphite-cellulose extracts for their commercial value would be a study of certain proprietary articles. Results obtained could be held to apply only to the particular material studied and these would lose their significance with any change in the process of manufacture. Our Committee therefore has confined its investigations to such as it believed would throw some light on the legitimacy of the analysis of sulphite-cellulose extracts by the official hide powder method of tannin analysis and to such others as might enable the Association to enforce any action it might take in the matter.

Inasmuch as the manufacturers of the domestic sulphite-cellu-

lose extracts had shown a lively interest in this question of analysis, the Chairman felt it only proper to give them an opportunity to present their side of the case for the consideration of the Committee. He, therefore, sent them a cordial invitation to present their views and any data in their possession bearing on the subject under investigation, in hopes that they might be willing to co-operate in securing a result which should be fairest to all concerned. In one case he received no reply for a long time and finally was told at a personal visit from a representative of the company that the company believed the Committee biased and not likely to give them a fair deal. Later, however, this company did send samples of their product to the Chairman, but so short a time before the Convention as to make detailed study impossible. In the other case he received a cordial invitation to visit the laboratory of the company and talk things over, with the assurance that he might use in his report such information as was presented for his consideration. He made the visit, had the talk, and on his return received a copy of the following letter from the President of the company to his superintendent. "As this work" (that shown the Chairman) "was incomplete and intended only as a guide for ourselves I do not consider it advisable to furnish him" (the Chairman) "with either samples or analyses. It also seems to me that as Mr. Small is one of a Committee that has been appointed to thoroughly investigate the matter of the tanning action produced by extracts made from sulphite liquors, that whether our analyses be good or bad they should not properly have very much weight with such a supposedly disinterested committee."

The Chairman sincerely regrets that the position taken by the sulphite-cellulose extract manufacturers makes it impossible for him to include in this report a statement from them of their views. He, however, has included such arguments as he has heard advanced. While the Committee has believed that it was its duty to draw conclusions, it has tried to present the facts so that the members of the Association might independently form their own opinions from the evidence.

Coming now to the work of the Committee; the question of the legitimacy of the analysis of sulphite-cellulose extracts by

the official hide powder method of tannin analysis depends in the first instance on our understanding of the intended purpose of the method. Two points of view are possible. Either, "A", we may believe the hide powder method of analysis should be used solely for the estimation in a given material as accurately as may be, of the content of tannin (understanding by this term, certain definite chemical compounds of characteristic individuality); or, "B", we may believe the hide powder method of analysis should be used to estimate the content of substances of any sort which under the conditions of the method can be absorbed by hide powder.

If we accept alternative "A", the question of the legitimacy of the analysis of sulphite-cellulose extracts by the official hide Powder method depends on whether these extracts contain the chemical individuals called tannins in the approximate amount shown by the method. What are the experimental facts? Sulphite-cellulose extracts give certain of the reactions of the tannins, such as precipitating solutions of gelatin (Bennett finds they do not, *Journal A. L. C. A.*, Vol. VI., p. 609), forming precipitates with the alkaloids, etc., but on the other hand they fail to give ***most*** of the characteristic reactions. No color reaction is given by sulphite-cellulose liquors with ferric salts. No red color is given with ammonia and ferro-cyanide. No precipitate is formed with bromin or with formaldehyd and hydrochloric acid. No precipitate is formed with tartar-emetic and salt. The above properties are really common knowledge but to avoid possible mistake, the statements made have been checked in the Chairman's laboratory and found correct for the sulphite-cellulose extracts tested. Also Mr. Veitch reports that "Several of the ordinary characteristic tests for tannin were applied to the sample of sulphite-cellulose extract, but in no case could a characteristic reaction for either a pyrogallol or catechol tannin be obtained. A precipitate was obtained with Gelatin and salt solution. This, together with the apparent tannin content obtained by the hide powder method were the only indications of the presence of tannin."

Further, no substance having the accepted properties of tannin can be extracted from sulphite-cellulose liquors with alcohol,

acetone or acetic ether. Mr. Kerr in a letter to the Chairman says "applying these solvents" (alcohol and acetic ether) "to sulphite-cellulose extracts we have found that while the alcohol dissolves out a considerable quantity of material, it does not give any of the characteristic reactions that tannin does after evaporating off the alcohol and redissolving the residue in water. It is true that upon adding gelatin it becomes cloudy but does not throw down a flocculent precipitate as is done by all tanning solutions of similar strength. We also find that ethyl acetate does not dissolve and separate this substance but takes out what appears to be resinous matter which is insoluble in distilled water after evaporating off the solvent."

Mr. Reed has reported as follows: "Undiluted sulphite-cellulose extract was digested with acetic ether for considerable time and filtered. Filtrate was evaporated, redissolved in acetic ether, filtered and again evaporated. Residue was dissolved in water, filtered, and tested with gelatin-salt solution for tannin with negative result. Also tested with ferric alum with negative result so far as a blue or black coloration. Exactly similar tests were made with acetone and alcohol as the solvents in place of acetic ether and with entirely negative results. True tannin-containing materials tested by these methods gave the most positive results."

The tannins have a fairly definite oxidation value in terms of permanganate as used in the Löwenthal method. The value of sulphite-cellulose extract is entirely outside the range of the tannins.

One explanation of the failure of sulphite-cellulose extracts to give up a material having the properties of the tannins has been advanced as follows: Sulphite-cellulose extracts are the result of a sulphiting process and therefore contain sulphited tannins similar to those found in sulphited quebracho. Two necessary corollaries of this explanation would seem to be that the coniferous woods from which the sulphite-cellulose liquors are obtained should contain tannin in appreciable amount and that the sulphite-cellulose extracts themselves should respond to such of the tests for tannin as do the sulphited-quebracho tannins. Experiments made in the Chairman's laboratory show that

neither of these corollaries is true and the explanation apparently fails to explain.

Possibly this discussion is unnecessary for the Chairman has found no one, even among those most favorably disposed to sulphite-cellulose extracts who cared to contend and undertake to prove experimentally that these extracts contain tannin or even sulphited tannin in appreciable amount. The Committee feels safe, therefore, in concluding that sulphite-cellulose extracts do not contain tannin in appreciable quantity and that consequently under alternative "A", sulphite-cellulose extracts are not legitimately analyzable by the official hide powder method of tannin analysis.

Turning now to alternative "B". This, for the sake of argument, was stated as broadly as possible but, as stated, is so broad as to be absurd. Who believes the method intended for the estimation of inorganic materials? Who believes it intended for the estimation of materials like glucose or starch which enter into no sort of combination with hide substance? To state this alternative so that it may be within the limit of possible acceptance by the Association it will become,—the method may be used for the estimation of vegetable substances which can unite with hide to form leather; or, better, since estimation involves measurement;—the method may be used in such cases as it estimates with approximate accuracy those substances of a vegetable nature which can combine with hide to make leather. This definition, limited as it is over the original statement, is much broader than "A" and seems to the Committee as broad as possible if the method is to retain any usefulness and not be reduced to an absurdity. Under this alternative we have to determine whether sulphite-cellulose extracts contain vegetable material capable of combining with hide to make leather and whether the amount of such material is estimated with reasonable accuracy by the hide powder method of analysis.

First; do sulphite-cellulose extracts contain vegetable material capable of combining with hide to make leather? It does not concern our purpose whether the leather is a merchantable commodity,—it is sufficient that it meet the definition of leather as hide so treated as to be imputrescible, pliable and opaque. Most

of the sulphite-cellulose extracts on the market contain so much aluminum or chromium compounds as to make the determination of this question somewhat difficult, but the Chairman was furnished with a sample of sulphite-cellulose extract containing only a magnesium base and was able to produce with it a product which answers to the above definition of leather. The several members of the Committee have tanned hide powder with sulphite-cellulose extract and found it to be combined with a certain percentage of organic material which could not be removed by ordinary washing. It seems to the Committee, therefore, that the evidence is conclusive that some at least of the sulphite-cellulose extracts do contain a certain amount of some vegetable materials which will actually combine with hide (not merely are absorbed by it) and make leather as defined above.

We have next to consider whether the amount of material in sulphite-cellulose extracts which will combine with hide to make leather is approximately represented by the amount absorbed by hide powder in the official method of tannin analysis. It is by no means a necessary corollary that the two are identical. The Chairman had occasion some time since to study a vegetable material for its tannin content and obtained certain liquors which, according to the hide powder method of analysis, contained 5 per cent. tannin but which nevertheless had absolutely no tanning or leather-forming action on hide. What is the evidence in the present case?

We have first the fact that a sulphite-cellulose extract which shows 25 per cent. tanning material by the hide powder method of analysis shows only 5 per cent. roughly by the Löwenthal method. This, however, is not particularly direct or valuable evidence on the point under consideration, for we have already seen that it is not probable that sulphite-cellulose extracts contain tannin or even a sulphited tannin. Now the Löwenthal method, while not a means of accurately measuring tannin does depend for its usefulness upon the fairly definite oxidation value of the tannins in terms of permanganate. If the tanning agent in sulphite-cellulose extract is not tannin, it is not to be expected that the Löwenthal value and the hide powder absorption value will agree.

The next bit of evidence at hand is that the amount of tanning

material in sulphite-cellulose extracts as shown by the hide powder method of analysis is more largely dependent upon the exact proportions employed than is the case with the common tannin-containing extracts. For instance, an oak bark extract, of high non-tannin content to correspond better with the sulphite-cellulose extract, and two sulphite-cellulose extracts were analyzed with varying amounts of hide powder. The following results were obtained:

	Oak bark		S. C. No. 1		S. C. No. 2	
	Wt.	%	Wt.	%	Wt.	%
Total solids	0.7403	46.38	0.7580	48.00	0.7896	49.68
Soluble solids	0.7086	44.40	0.7625	48.28	0.7945	49.99
Non-tans 1/2 h-p	0.3453	21.63	0.4738	30.00	0.4879	30.70
Non-tans 1 h-p	0.3118	19.54	0.3972	25.15	0.4097	25.78
Non-tans 3/2 h-p	0.2983	18.69	0.3645	23.08	0.3853	24.24
Tannin 1/2 h-p	0.3633	22.77	0.2887	18.28	0.3066	19.29
Tannin 1 h-p	0.3968	24.86	0.3653	23.13	0.3848	24.21
Tannin 3/2 h-p	0.4103	25.71	0.3980	25.20	0.4092	25.75
Total difference	0.0470	2.94	0.1093	6.92	0.1026	6.46

The variation in the amount of material absorbed from the sulphite-cellulose extracts when different amounts of hide powder are used is more than double that found when a tannin-containing material is analyzed. So far as it goes, this seems to be evidence that in the analysis of sulphite-cellulose extracts, much more material is physically absorbed rather than combined, than in the analysis of tannin-containing extracts and that consequently the accuracy of the estimation by the hide powder method of the quantity of material in sulphite-cellulose extracts which will *combine* with hide is decidedly open to question.

A somewhat similar series of experiments was conducted by Mr. Reed except that he used different proportions of hide to liquor and different times of contact. His report is as follows:

EXPERIMENT No. 1.

	Barkometer Degrees
Tan liquor ½ oak bark, ½ chestnut	27
Liquor—glutrin	26

400 cc. of above liquors shaken with 24 gms. wet chromed powder—equivalent to 6.5 gms. absolutely dry,—for a period of 10 hours;—the hide powder being in contact with the liquors in all for four days.

Analysis of liquors before and after tanning.

	Oak and chestnut New	Oak and chestnut Sap.	Glutrin New	Glutrin Sap.
Barkometer	27°	18°	26°	22½°
Total solids	6.47	4.45	5.96	5.13
Soluble solids	6.00	4.16	5.96	5.13
Insolubles	0.47	0.29	0.00	0.00
Non-tans	2.49	2.56	3.17	3.17
Tannin	3.51	1.60	2.79	1.96

	Oak and chestnut	Glutrin
Per cent. barkom. sappage	31	13.5
Per cent. Tannin sappage	54.4	29.8
Hide substance in absolutely dry leather	51.8	69.0

EXPERIMENT NO. 2.

	Barkometer Degrees
Tan liquor ½ oak bark, ½ chestnut	27
Liquor, glutrin	31

500 cc. of these liquors shaken for one hour with 120 gm. wet hide—equivalent to 33 gms. absolutely dry hide.

Analysis of above before and after—

	Oak and Chestnut		Glutrin	
Barkometer	27°	13°	31°	22°
Total solids	6.49	2.93	7.13	4.85
Soluble solids	6.08	2.70	7.13	4.76
Insolubles	0.41	0.23	0.00	0.09
Non-tans	2.52	2.09	3 54	3.16
Tannin	3.56	0.61	3.59	1.60
Per cent. barkom. sappage	52		29	
Per cent. Tannin sappage	82.9		55.4	

NOTE—In oak-chestnut liquor new—official amount of hide powder removed all tan, but to remove all from the glutrin new it required 60 gms. wet powder—16.5 gms. dry. In oak-chestnut liq. sap, 30 gms. wet hide removed all tan but it required 48 gms. wet hide to remove all "tan" from glutrin sap.

In this series of results the failure of the sulphite-cellulose extracts to give up to the hide powder anything like the amount of combining material supposedly present as shown by the hide powder method of analysis is most pronounced. Unfortunately for the conclusiveness of the proof that this result is due to lack of combining material, another explanation is possible, viz.: that the combining material in sulphite-cellulose extracts has a low combining-value with hide. As will be shown later on in this

report, hide apparently can combine with a much smaller weight of the combining material in sulphite-cellulose extracts than of tannin; although here again our statement must be qualified, as the time of contact may prove to be an important factor. Certainly sulphite-cellulose extracts under similar conditions so far as tested will combine with hide to a much more limited extent than tannin-containing extracts.

A direct comparison of the leather-forming value of sulphite-cellulose extracts and tannin-containing extracts was made by experiments conducted along lines suggested some years ago by Dr. Parker for estimating the leather-forming value of different tanning materials. *Collegium,* No. 88, p. 363.

Mr. Kerr as long ago as June, 1906, had carried out tests of this sort and in a letter to the Chairman has given an account of some of the experiments carried on in his laboratory as follows:

Method employed for making test for weight-yield of extracts with hide powder.

Ten grams of screened hide powder (screened through 20 inch screen, dust passing through being rejected) is macerated with 55 cc. of distilled water for three hours, with occasional stirring to insure uniform saturation.

Two hundred and fifty cc. of solution of extract to be tested, containing 5 per cent. tannin, made up with hot water (80° C.) and allowed to cool slowly.

To tan the hide powder a portion of the solution is added to the macerated powder, which is contained in a beaker (covered during maceration) and stirred well. It is then added to remainder of liquor, care being taken to get all the hide powder out of the beaker into the liquor. The magma is then shaken for thirty minutes constantly, and aferwards for ten minute periods each hour for three hours. It is then allowed to stand for twenty-one hours.

Upon completion of tanning, the tanned hide powder is squeezed out and passed through a wringer and weighed. It is then divided into two equal portions and one dried. The other is then rubbed into powder and placed in a 3″ funnel, plugged with a small cotton plug, and washed with 500 cc. of cold dis-

tilled water, and again squeezed, wrung, weighed and the wet weight noted. It is then dried and weighed, which weight multiplied by 2, gives the leather or tanned weight.

Weight yield made as above of

Hemlock extract.
Liquid clarified quebracho.
Ordinary solid quebracho.
Ordinary chestnut.
Clarified chestnut.
Sulphite-cellulose extract.

For solutions volume 500 cc.

88.25 Grams Hemlock extract.
61.10 Grams Liquid clarified quebracho.
36.10 Grams Ordinary solid quebracho.
70.60 Grams Ordinary chestnut.
72.00 Grams Clarified chestnut.
100.00 Grams Sulphite-cellulose extract.

The solutions were cooled and allowed to stand over night and only the supernatant liquor used for tanning.

Gravity of liquor used for tanning:

Hemlock	1.025	Appearance very cloudy
Liquid clarified quebracho	1.021	" " "
Ordinary solid quebracho	1.019	" " muddy
Ordinary chestnut	1.029	" clear
Clarified chestnut	1.030	" cloudy
Sulphite-cellulose extract	1.0475	" clear

Gravity of liquors after tanning:

Hemlock	1.011	Appearance almost clear
Liquid clarified quebracho	1.0075	" clear
Ordinary solid quebracho	1.0055	" "
Ordinary chestnut	1.013	" almost clear
Clarified chestnut	1.0135	" cloudy
Sulphite-cellulose extract	1.043	" clear

	Specific gravity			Per cent. absorbed by difference of gravity
	Before tanning	After tanning	Loss	
Hemlock	1.025	1.011	0.014	56.00
Liquid clarified quebracho	1.021	1.0075	0.0135	64.25
Ordinary solid quebracho	1.019	1.0055	0.0135	71.00
Ordinary chestnut	1.029	1.013	0.016	55.10
Clarified chestnut	1.030	1.0135	0.0165	55.00
Sulphite-cellulose extract	1.0475	1.043	0.0045	9.50

WEIGHT OF UNWASHED TANNED HIDE POWDER.

	Wet grams	Dry grams
Hemlock	34.51	18.84
Liquid clarified quebracho	36.23	19.60
Ordinary solid quebracho	36.59	20.10
Ordinary chestnut	33.55	18.74
Clarified chestnut	34.62	19.42
Sulphite-cellulose	27.68	13.36

WEIGHT OF TANNED HIDE POWDER AFTER WASHING AND DRYING.

	Grams	Loss from washing Grams
Hemlock	17.68	1.16
Liquid clarified quebracho	18.22	1.38
Ordinary solid quebracho	18.76	1.34
Ordinary chestnut	17.78	0.86
Clarified chestnut	18.00	1.42
Sulphite-cellulose extract	11.54	1.82

Note:—The weights of the hemlock and ordinary solid quebracho are obviously too high on account of the entanglement and retention of the insoluble matter held in suspension by the liquors used for tanning. No practicable method of getting these liquors clear presented itself at this time.

Confirming other tests, it seems conclusive that sulphite-cellulose extract possesses but little value as a tanning material, the hide fixing but one-fifth as much as the lowest of the other materials.

A report of similar experimental work was made by Mr. Veitch as follows:

MEMORANDA ON EXPERIMENTS UPON SULPHITE-CELLULOSE LIQUORS FOR F. H. SMALL, A. L. C. A., 1912.

(Material used is sulphite-cellulose extract.)

Analysis by the official method gave the following results:

	Per cent.
Soluble solids	48.9
Non-tannins	25.7
Tannin	23.2
Non-tannins (using unchromed hide powder)	26.2

Ten gms. of dry standard American hide powder were washed twice by shaking for 5 minutes in a shaking machine with 200 cc. of water and filtered. The hide powder was then shaken with 200 cc. of 0.3 per cent. (considering the sulphite-cellulose extract

to contain 25 per cent. tannin) tannin solution, for 30 min. and filtered. The partially tanned powder was then shaken with 200 cc. of 3 per cent. tannin solution for 2 hrs., and filtered; then, finally, shaken for 4 hrs. in a 6 per cent. tannin solution and allowed to stand over night, then filtered. The tanned hide powder was then air dried and weighed. It gave 14.28 gms. It was then washed four times with 150 cc. of water containing a trace of acetic acid by shaking in a shaking machine for 15 min., then dried and weighed. The weight obtained was 11.2 gms. Soluble material was still coming out at the end of this washing. The loss at this stage was 3.08 gms. Nitrogen was determined at this point and showed 11.34 per cent., giving the hide substance as 63.5 per cent. The residue was then extracted, first with cold water and finally with water at 50° C. The material extracted in this way amounted to a little over 0.5 gm. and the total loss from the tanned hide powder was thus increased to 3.5 gms. Allowing the loss of 1 gm. of dry hide in the first washing of the hide powder, this powder as tanned would contain 9 gms. of hide, and 5.28 gms. absorbed substance. On washing and extracting 3.5 gms. were removed, leaving about 1.78 gms. of absorbed material in the hide. After further extraction of the tanned hide powder a point was reached at which a small amount of coloring matter still came out, but the extract gave no reaction for soluble hide or tannin.

A similar set of experiments was carried through a few weeks ago by Mr. Hayes under the Chairman's direction. The procedure was outlined as follows:

Put 100 gms. approx. hide powder in glass jar. Determine moisture by drying 5 gms.

Put the equivalent of 10 gms. absolutely dry hide powder from jar in shaker bottle. Add 150 cc. water and churn ½ hour.

Have ready 500 cc. of exactly 10 per cent. solution of extract.

Add	50 cc.	of this solution and churn	½ hr.
"	50	" " "	½ hr.
"	50	" " "	½ hr.
"	50	" " "	1 hr.
"	50	" " "	1 hr.
"	50	" " "	2 hrs.
"	50	" " "	4 hrs.
	350 cc.		9½ hrs.

Throw on funnel,—neck plugged with cotton wool,—washing all of hide powder on funnel with percolate; press down with fingers and let drain 18 hours. Keep covered. Transfer to porcelain dish and weigh. Dry 10 gms. to determine moisture.

Put exactly 20 gms. back in funnel and wash with 2 liters distilled water at 40° C. Remove to porcelain dish; again weigh and dry 10 gms. for moisture. The results of the experiments were the following:

YIELD OF UNWASHED LEATHER.

	Weight gms.	Per cent. gain.
S. C. extract I	19.89	98.9
S. C. extract II	19.85	98 5
Chestnut wood extract	25.15	151.5
Oak bark	26.62	166.2

YIELD OF WASHED LEATHER

	Weight gms.	Per cent. gain.
S. C. extract I	13.73	37.3
S. C. extract II	13.01	30.1
Chestnut wood extract	17.73	77.3
Oak bark	17.81	78.1

These results seem to establish that under similar conditions as shown by the hide powder method of analysis the combining value of the sulphite-cellulose extracts is not much more than half that of tannin-containing extracts.

As bearing on the particular point under discussion, viz.: Whether the hide powder method of analysis accurately estimates the amount of leather-forming material in sulphite-cellulose extracts, the Chairman must admit that the evidence presented is rather circumstantial than positive. He believes, however, that it suffices to cast a reasonable doubt upon the accuracy of the estimation.

The Committee therefore finds that sulphite-cellulose extracts contain a percentage of some material which can combine with hide to make leather as defined;—that under like conditions the amount of this material which will combine with hide is much less than will combine from tannin-containing extracts;—that the quantitative estimation of the combining material in sulphite-cellulose extracts by the hide powder method is of doubtful accuracy. Your Committee is therefore of the opinion that in view of the above facts the Association, if it accept alternative

"B", should resolve that until such time as it shall be shown that sulphite-cellulose extracts contain leather-forming material of the same order of value as tannin, which material is estimated with approximate accuracy by the hide powder method of analysis, the Association will refuse to sanction the use of the method for this purpose. Any action the Association may take to the above end will be merely safeguarding its own interests,—refusing to sanction the use of its methods for conveying what it believes to be false information It can in no sense affect any agreement between buyer and seller to accept as a basis of sale a value found by submitting sulphite-cellulose extracts to the procedure used in tannin analysis.

As between alternatives "A" and "B" your Committee believes that the official method of tannin analysis was intended to be used for the estimation of the *tannin* content of vegetable materials or extracts derived from them, *i. e.*—that the legitimacy of the analysis of a material should be established under alternative "A", and that the method should be so defined and its use so limited as recommended in the report of the Committee on the revision of the hide powder method.

Should the Association conclude to take action along the lines above recommended by this Committee it is evident that a means of detecting sulphite-cellulose extracts must be at hand that the members may be able to conform to the ruling of the Association.

In the Committee's knowledge, no test or combination of tests has been discovered which is superior to that published by Procter and Hirst, using aniline and hydrochloric acid for qualitative detection and the Löwenthal method for quantitative estimation as recommended by them,—*Journal A. L. C. A.*, 1909, pp 147. 149; reprinted from *J. S. C. I.*

The aniline test has been tried out by Mr. Hayes in the Chairman's laboratory on many samples of sulphite-cellulose extracts, both straight and in admixture and in no case has it failed to give a test when as much as 5 per cent. of sulphite-cellulose extract was known to be present. One precaution is necessary, viz.: To make sure the aniline is pure and reasonably fresh. An old sample used in the Chairman's laboratory led to confusing results because of giving a precipitate even when no trace of

sulphite-cellulose liquor was present. Mr. Eachus has reported a similar experience.

Mr. Hayes in the Chairman's laboratory devoted a large amount of time to an attempt to work out some means of affecting a quantitative separation of sulphite-cellulose extract from tannin-containing extracts, but with only negative results. It would seem for instance, since sulphite-cellulose extracts are not precipitated by bromin or tartar emetic and salt that it would be a simple matter to precipitate the catechol tannins with bromin, the pyrogallol tannins with tartar emetic and salt and estimate the sulphite-cellulose extract in the filtrate; but practically it does not work out as the reactive materials in sulphite-cellulose extracts are co-precipitated with the tannins when in admixture, a fact which may be used as an argument in favor of their being related compounds. The most helpful test discovered by Mr. Hayes was the following: A mixture is made of 40 cc. of a 2 per cent. gelatin solution and 30 cc. of glacial acetic acid. Seven cc. of the reagent is added to 10 cc. of the solution to be tested, this latter being of regular analytical strength. If wood pulp liquor is present, a precipitate is formed which persists even on heating. This has been tested carefully and so far as tested has been found accurate.

To sum up, the Committee finds that the evidence supports the view that sulphite-cellulose extracts contain no appreciable amount of tannin or sulphited tannin and that they are therefore not legitimately analyzable by a method of *tannin* analysis;—that sulphite-cellulose extracts do contain some material which will combine with hide and make leather as defined, that the combining value of this material is much less than that of tannin under like conditions, that it is at least doubtful whether the hide powder method of tannin analysis estimates the quantity of this material present in sulphite-cellulose extract with even approximate accuracy.

Your Committee recommends that this Association resolve that the official method of tannin analysis of the Association shall be limited in its use to the analysis of vegetable materials or extracts therefrom which contain tannin and to those cases where the method estimates with reasonable accuracy the probable content of tannin.

DISCUSSION.

This report of the discussion has been considerably condensed, but it is believed that nothing of serious importance has been omitted.—EDITOR.

MR. HURT:—I agree with Mr. Small in a great many things that he said, but I wish to call your attention to some evidence on the question as to whether the material in the sulphite-cellulose liquor combines with hide and forms leather, or as to whether there is any real tannin in sulphite liquor. I have worked with the material for seven years, and my experience has been that the liquor must be carefully and properly treated and prepared. If this is done, good leather can be made. There is a true tannin in sulphite liquor, entirely different from the tannin in other materials. To test the leather-making qualities by comparison, I took two samples of sulphite liquor, and one sample of chestnut extract, determined the tannin in the three, took the hide powder which was used in the determination of the tannin, soaked it in water at 105°-110° F. for 24 hours, and then extracted it with water to a liter, determined the amount of the total soluble matter in the hide after treatment with sulphite liquor and with chestnut extract, and corrected it for the non-tannin content of the squeezed hide. (The first trial with sulphite extract No. 2 gave a bad non-tan, so a second trial was made.) Results in the table.

Extract	Grams wet hide taken	Per cent. "tannin" found	Per cent. soluble matter extracted	Per cent. of total tannin extracted
Sulphite, No. 1	70	25.83	6.00	23.22
Sulphite, No. 2	70	25.86	5.13	19.83
Sulphite, No. 2 (b)	80	26.25	4.46	16.99
Chestnut	60	27.81	10.26	36.89

This work was done in duplicate, and shows conclusively that the tannin of chestnut extract after treatment with hide is more soluble than the tannin of sulphite extract. In view of this I do not see how the committee can take their position in the matter. I would be glad to show you samples of leather which I tanned myself, and which have stood for five years. Sulphite

liquor, properly prepared, produces a leather which is stronger than any leather which I have ever seen tanned with any other material, which shows absolutely no signs of decay, and which by actual test has proved to be outlasting both hemlock and oak leathers.

MR. MOSSER:—I would like to ask Mr. Small if they made any ash determinations.

MR. SMALL:—I did not make any ash tests of the tanned hide powder, but I did of the samples of leather which I tanned. One sample showed an ash content of only 1.2 per cent., and as the extract with which this was tanned contained only a magnesia base, there was no inorganic material present in the sulphite-cellulose extract that could be responsible for the tannage obtained. An ash content of 1.2 per cent. is really not much above the normal ash content of a regular tannin-tanned piece of leather.

MR. TOUSEY:—Some eighteen years ago I was one of the organizers of the Anglo-American Canaigre Company, which had for its purpose the cultivation of the canaigre root and the manufacture of an extract from it. Mr. John Blair made some experiments for us, and a number of extracts of different kinds which we had analyzed by Professor Trimble of the University of Pennsylvania. He reported that they contained no tannin and were therefore not commercially valuable. We made up some of this extract and tanned some calf-skins and some sole leather with it. We had those leathers made up into shoes and distributed around, and I wore a pair of them for a year.

When we started to place our Muskegon extract on the market, for instance, I went to a tanner and explained to him what it was, and he said "All right, send me a barrel, I will try anything once." In several instances we got contracts. Suppose the tanner had said "That fellow said his extract ran 28 to 30 per cent. tan; I wonder if it does," and sent a sample down to Mr. Reed. Mr. Reed comes back and says "It does not contain any tan." Where are we? This extract, as Mr. Hurt says, will make leather, is making leather to-day, and has made leather.

This Association, I believe—and of course it is true—was formed for the purpose of advancing all the interests of the

tanning trade. I remember two years ago your President, Mr. Wilson, in his speech at the banquet spoke of the advances which had been made by the tanning chemists; that some years ago they were held in rather small repute, but they have grown out of that. It seems to me that when something new comes up, something that really has some merit and some value, that it certainly should be treated with charity, and given every chance by this Association.

MR. DICKERSON:—Of course, as you all know, Mr. Tousey and I are connected with the Muskegon Extract Company, which is one of the companies making sulphite-cellulose extract in this country. Naturally all our tests have been made with that material, but I think it applies in a general way to a waste sulphite liquor that is properly treated and prepared for tanning material.

Now in the report which Mr. Small has submitted he made the point that the extracts to-day on the market in this country were proprietary articles and that they contained certain matters —referring in that respect to the inorganic bases which they contained. We have quebracho extracts on the market under various brands that contain inorganic bases, some contain soda alone, some contain soda and aluminum, some contain chromium, but nothing is said about those being proprietary, and they are analyzed as quebracho extracts. It seems to me that an extract made from waste sulphite liquor, should not have that point raised against it and be branded as a proprietary article, simply because it is made under certain processes which involve the incorporation of inorganic bases in the extract. That same point might be made against a great many extracts, I imagine.

MR. SMALL:—I did not classify sulphite-cellulose extracts as proprietary articles for the reason that they do or do not contain certain inorganic constituents. I stated that inasmuch as the manufacturers of the sulphite-cellulose extracts claim that the suitability of these extracts for making leather is practically wholly dependent upon the specific treatment given the pulp liquors by the extract manufacturers,—the finished product,— the sulphite-cellulose extract,—is a proprietary article so far as concerns its commercial application to the making of leather.

I argued, therefore, that the commercial usefulness of sulphite-cellulose extracts is a subject for individual study and not a proper subject for investigation by the Association as a body, since the Association would in the event be compelled to pass upon the merits of an individual manufacturer's product.

MR. DICKERSON:—My only object in saying what I have in connection with that particular feature of the case is that the same thing is claimed, I believe, for different quebrachos and different extracts of other kinds. The manufacturers of them claim that their different processes give them features that make them more valuable than other manufactured extracts of the same kind.

MR. SMALL:—Quite true, but this Association has never passed judgment on the commercial value of sulphited quebracho extracts.

MR. DICKERSON:—Are we discussing a concentrated waste sulphite liquor, or are we discussing an extract made from a waste sulphite liquor as a base? We admit and have always stated that a concentrated waste sulphite liquor has no tanning value alone, compared with a prepared extract. It is the method of treatment which makes it available as a tanning material, and the prepared extract is what is submitted to the tanner for his tanning purposes, and that is what the chemist has to analyze. Now is the Association going to pass upon a concentrated waste sulphite liquor, which we admit and state has a very inferior tanning value to a properly prepared material, or is it passing upon the extract as submitted to the tanner?

MR. SMALL:—The committee has taken the ground that all it can be expected to pass upon is the method by which this material shall be valued analytically. If the manufacturers of the sulphite-cellulose extracts and the users of them wish to have the material put through the procedure of a tannin analysis by the hide powder method, the Association has absolutely nothing whatever to say in the matter. If, however, the manufacturer of the extract or anybody else asks the Association to put it through that procedure and report that it contains a certain amount of tannin or that it contains a certain amount of leather-forming material, when the Association believes that it

contains neither in the amount shown by the analytical figures, then it seems to me that the Association is perfectly justified in taking the attitude that the committee has taken, and it is from that point of view that the committee has undertaken its investigation, and it is on that ground alone that the committee has made its recommendation.

MR. DICKERSON:—In view of Mr. Small's explanation of the matter, I think it comes down to this question: Is there enough specific and definite knowledge to-day regarding the true nature of the tannins? Can any one here state that there are not tannins which will just as truly combine with hide substance as the tannin which is recognized by the color reactions which Mr. Small has stated were used by the committee in their tests?

MR. SMALL:—The Committee recognizes that there are other tanning materials, and other tanning materials of an organic nature. There is quinone tanned leather; there is formaldehyde tanned leather, but no one has come to us and asked us to report quinone as tannin or to report formaldehyde as tannin.

MR. DICKERSON:—That is true. We know what those substances are; but we have in waste sulphite liquor a material of which very little is known. I have a piece of leather here which was tanned four or five years ago by Mr. Tousey and myself personally, and I will pass this around. I will make an affidavit to the effect that there is absolutely nothing in that but an extract made from waste sulphite liquor and that piece of leather is between four and five years old. Now the material to which Mr. Tousey referred in his remarks; which Mr. Blair made up into an extract and which Professor Trimble pronounced as having only a trace of available tannin, was made from the canaigre itself by a special process and made into an extract which made leather, but it did not show tannin as would be indicated by these color reactions. It seems to me that it is getting down to very narrow limits on the construction of tannin. What the tanner wants to know is what will combine with his hide substance and make leather. Of course if they are going to define tannin, reduce it to a question of what is tannin, I should think the body of your method ought to embody a specific definition of what that tannin was, re-

ferred to in the title, because in the body of the method, under the head of "Tannin," it says the matter indicated as tannin shall be the difference between the total soluble solids and the non-tans, or the amount absorbed by hide, and that is what the tanner really gets.

I was the gentleman who called on Mr. Small a few weeks ago, to whom he referred in his report. We had no technical data to submit at that time; we had nothing but tannery results, and as Mr. Small has said, the committee had nothing to do with tannery results. It was technical data they were after. Since that time we have had some work done by Mr. Hoppenstedt, of Buffalo. Samples of waste sulphite liquor extract were submitted to him alone and in combination with quebracho, and they were tested out in the following manner:

Samples of sulphite-cellulose and quebracho extract were first analyzed by the official method, and then in accordance with the results obtained, solutions of the respective extracts, of one liter each, were made up to contain 2.8 per cent. of tanning matter, or 28 gms. of tanning matter to the liter. Lots of 20 grams each of air-dry hide powder were placed in 500 cc. Erlenmeyer flasks and thoroughly soaked over night with 150 cc. of distilled water. They were then slowly tanned by adding, at various intervals, equal measured amounts of the respective extract solutions, and during the tannage equal amounts of the spent liquor were removed to make room for the fresh solution. The flasks were gently shaken after each addition of fresh liquor and also frequently during tannage. Seven days were allowed for the tannage, and a whole liter of extract solution was given to each lot. Thus each lot of 20 grams of air-dry hide powder received 28 grams of tanning matter. After tannage, the lots were thoroughly washed with distilled water in the same flasks in which they had been tanned. The washing covered a period of three days and was continued until practically no more soluble matter was extracted. The leather was then collected on linen and slowly dried at room temperature. When dry, the leather was weighed. Moisture determinations were made and the nitrogen determined on the absolutely dry leather. In order to determine also how firmly

the tanning matter was held by the fiber, the air-dry leather was extracted with water at 50 degrees C. During the entire work the two lots received absolutely the same treatment and only differed in the extract used for tanning. Five such tests were made. The first test was made with sulphite-cellulose extract; the second, clarified quebracho; the third, ordinary quebracho; the fourth, a blend of two-thirds ordinary quebracho and one-third sulphite-cellulose extract; the fifth, half and half of the two materials. The blends were made on a basis of total solids, but in making up the liter of tanning solution, 28 grams of tannin were present in each case. Analyses of the extracts and blends follow; all figures percentages:

	Muskegon extract No. 133	Clarified quebracho extract	Ordinary quebracho extract solid	⅔ ord. queb. ⅓ muskegon		½ ord. queb. ½ muskegon	
				calc.	found	calc.	found
Total solids	49.68	43.14	79.33	49.68	49.68	49.68	49.68
Reds	0.14	0.47	5.91	2.52	1.31	1.92	0.40
Non-tans	21.56	5.94	6.69	9.98	11.51	12.88	15.15
Tannin	27.98	36.73	66.73	37.18	36.86	34.88	34.13

Nitrogen determinations were made, and in the following table these are given, with the gains, and also the results of the examination of the water extract obtained from the tanned hide powder at 50° C.

	Muskegon extract	Clarified quebracho	Ordinary quebracho	⅔ ord. queb. ⅓ muskegon	½ ord queb. ½ muskegon
Nitrogen	11.12	10.05	9.72	9.06	8.74
Hide substance	62.47	56.46	54.61	50.90	49.10
Tanning matter	37.53	43.54	45.39	49.10	50.90
Gain	160.08	177.12	183.12	196.46	203.67
WATER EXTRACT AT 50° C.					
Total soluble	3.35	5.41	5.50	5.12	4.64
Non-tans	0.74	0.89	0.99	0.98	0.87
Tanning matter	2.61	4.52	4.51	4.14	3.77

(Report signed, A. W. HOPPENSTEDT.)

Here we have an instance showing that the hide powder tanned with the waste sulphite liquor extract was more thoroughly combined, the tanning matter was more firmly bound, than the quebracho tannin. It would seem to me that in view of the results that have been gotten, and the admitted lack of knowledge of the true character of tannins, that no one here

would be willing to get up and go on record and say that there is no tannin of any kind in these sulphite-cellulose extracts. It would seem to me that something added to the present official method covering the analysis of waste sulphite liquors would be better than such a drastic ruling as the recommendation of the committee.

Mr. Yocum:—I feel that the report of the Committee is rather severe, and that the object of this Association is primarily to work along lines such as will be of interest and value to the tanner, and in view of the fact that tanners are using these sulphite products, it is up to this Association to provide some means of measuring it. I quite agree with Mr. Small, that our present official method of tannin determination is probably very inaccurate as a measure of the combining material in these sulphite-cellulose extracts, but at the same time, with a business as large and growing as this seems to be, the Association should make some rule that will permit of the valuation of these extracts when it is understood both by the tanner and the extract manufacturer what the material is. I have here a memorandum that I am going to suggest be added as a clause to the revised method of the Association.

"Materials not generally conceded to be true tannin, but containing matter absorbed by hide powder, shall be analyzed by the same method employed for the generally accepted tannin materials, and be reported as 'material absorbed by hide';" making it specific as far as can be that it is not a true tannin material, and so report it.

Mr. Balderston:—I should like to see this paragraph which Mr. Yocum has suggested adopted. We have no other method of analysis that will tell us anything about it, and if we analyze it fairly and honestly and write at the bottom "This is cellulose extract and contains so much stuff absorbed by hide powder," or if it is a blend say, "This material contains sulphite-cellulose," I think it would be the fair and honest thing.

Mr. Loveland:—I would just like to add a word in agreement with what Mr. Yocum and Dr. Balderston have said. As I understand this discussion, it does not hinge upon the value

of any given material in comparison with any other material, but upon the value of material in comparison with itself, and that we should not take the value of a sulphite-cellulose extract and compare it with the value of a quebracho extract as a tanning material, but that we should give these gentlemen a value of their material in comparison with itself by our official method. It does not make any particular difference how we analyze the substance if we get concordant results. For instance, if the tannin unit of quebracho is four cents to-day, and we find 60 per cent. tannin in that quebracho, and to-morrow morning we change our analysis so it only contains 30 per cent., the value of that quebracho extract instead of being four cents to the tannin unit will be eight cents. They will sell it to-morrow morning at the same cost as they sell it to-day. The tanners are using this, and they are going to use it, and if we place value on it in comparison with itself, I think we are working no injustice to ourselves or the trade.

MR. SAXE:—The sale of these extracts is increasing largely in this country. It is being made in England; it is being made on the continent, and the English have recognized that it makes a pretty good blend. Now whether it is a true tanning material or not, I do not know. I am no chemist, but I do know it makes leather, and that is what interests the tanner.

MR. MOSSER:—I think the idea of this Association is to adopt methods that will give the greatest concordance in results. According to the Committee's report on comparative analysis, the greatest difference in all the extracts between the members was in the sulphite-cellulose extract. It seems to me that the method that is used for tannins does not apply to the sulphite-cellulose extracts with as great accuracy as it does to analyses of the natural tannins. If we are going to recognize sulphite-cellulose extract, I think we will have to have a method that will bring it in greater concordance.

MR. DICKERSON:—In regard to those analyses I believe that some of the chemists will bear me out in what I say. I think that as Mr. Alsop has previously said, if you could standardize the chemists on that work—for it is purely an empirical method—and if you could get every one working it in absolutely the

same manner, as to temperature and manipulation of every part of the method you would get concordant results, and I believe that the proper percentage of acidity in hide powder will give absolutely concordant results on analysis of waste sulphite liquor extracts.

MR. REED:—I work as carefully as I can day in and day out with my methods and I cannot duplicate my results on sulphite-cellulose extract; that is from day to day they will not give the same.

MR. BALDERSTON:—I think we all wish most heartily that we could have a good way of analyzing these liquors, a way that would always give concordant results; but while we are waiting for one like that let us use the best we have got.

MR. SMALL:—There seems to be evident a feeling that the committee in its report has done a decided injustice to a growing industry. This certainly was farthest from the intention of the committee. In fact, to avoid this very charge the committee was careful to invite the manufacturers of the sulphite-cellulose extracts to confer with it so that if possible a result satisfactory to all concerned might be arrived at. The manufacturers, however, failed to show any marked desire to co-operate to this end and the committee was forced to reach independently such conclusions as it believed the evidence demanded. In the face of the evidence the committee believed the injustice would be to the Association did it ask you to analyze sulphite-cellulose extracts by the hide powder method and report the apparent tannin figure as so much tannin or matter absorbable by hide, thereby giving the impression that a material of the same order of leather-forming value as tannin was being estimated.

Mr. Delaney inquired whether extracts made from chestnut wood or other material extracted under pressure might not contain materials which would respond to the Procter-Hirst aniline test. Mr. Reed and Mr. Yocum thought not.

The subject was referred to the Council, no vote having been taken on the recommendation of the Committee nor on Mr. Yocum's amendment.

DISCUSSION ON METHODS OF TANNIN ANALYSIS.[1]

MR. F. H. SMALL:—As one of the Committee which revised the method of tannin analysis, I am glad of the opportunity to say a few words in reply to the criticisms contained in the report, a summary of which you have just heard.

In the first place Mr. Alsop remarks that "it might be well to consider Mr. Faust's suggestion that the solution be allowed to stand for one hour before cooling in water. I think that something should be in the method in reference to agitating the solutions while cooling them in water, and especially during the first part of the operation, as all of our experiments point to the fact that there is little difference between the methods if this is done, even when cooling with water considerably below 19 degrees C." If you will go through the reports of the committees, which in years past have studied the question of the cooling of solutions for analysis, you will find that they show that if the analysis solution is brought to a definite temperature and kept there for a reasonable length of time, an equilibrium as regards the content of insoluble matter is reached which is essentially the same regardless of the route by which the solution is brought to the temperature. The time required to reach this condition of equilibrium is mainly dependent on the difference between the minimum and the final temperatures. That being the case, your committee believed that if they required that the analysis solution be cooled in water at a temperature not lower than 19 degrees, the result would be to bring the solution to 20 degrees without any part being cooled to a temperature sufficiently below 20 degrees to throw out an amount of insoluble material appreciably in excess of the normal. Thus the condition of permanent equilibrium would be rapidly reached. The method was revised as stated with the particular aim of avoiding irregularities due to the more or less vigorous or constant agitation of the solutions in water at temperatures considerably below 20°.

With regard to the item under "Soluble Solids": where "several of the collaborators remark upon the difficulty of keeping solutions within the prescribed temperature limits during filtration,

[1] Ninth Annual Meeting, Washington, Dec. 6, 1912, following the reading of the report of Committee on Comparative Analysis, JOURNAL, October, 1912.

and also regard keeping the solutions to be filtered at 20 degrees as very troublesome, and one or two as unnecessary;" I know from my commercial experience in making tannin analyses that at the present time the widest variation in results in different laboratories on tanning materials which contain any considerable amount of insolubles is in the insoluble figure. While I have no opportunity for knowing the exact reason for this, I have no doubt in my own mind but that a considerable amount, if not the major amount, of this difference is due to a failure to keep the solutions at 20 degrees. Of course when the insoluble content is small; temperature differences make very little difference in the insolubles percentage; but when the insoluble content is reatively large as in the case of a myrobalan extract or an oak bark or a hemlock, temperature differences lead to very appreciable analytical differences. If you will look at the tables of the Committee report you will find in the case of the quebracho and of the hemlock samples that the analytical difference is widest in the insolubles item. Therefore, speaking for myself, because I have not had any opportunity to consult any of the other members of the Revision Committee,—I would like to insist that this is one of the most important items in the revision of the method as advocated by the committee. The suggestion on page 545, that the hide is not sufficiently chromed by the method suggested by the committee is probably a perfectly valid criticism. I think the committee probably was at fault in not specifying a definite time for soaking the hide powder, and also possibly at fault in not suggesting a slightly longer time for chroming. The committee based its suggestion on the reports of the committees in past years that had considered the subject of rapid chroming, and one of these committees, on which I think Mr. Alsop took a very active part, found that a rapid chroming of one hour was sufficient.

Also I think that the criticism with regard to the acidity of the hide powder is a decidedly wise one, and that there should be incorporated in the method a statement of an official method for determining the acidity of the hide powder, and also for bringing the acidity of a hide powder which is outside the prescribed limits to the acidity called for.

With regard to the extraction of materials the criticism is wholly destructive without offering any suggestion as to how matters may be remedied. I believe that the recommendation of the Revision Committee is correct and desirable, although I do think that probably a provision whereby it is permissible to use 50 cc. throughout is a needful one.

MR. ALSOP:—Mr. President, I say in this report: "A majority of the analysts collaborating in these tests made no comments whatever upon the proposed method, and the others were generally very brief;" so that very largely these opinions here are my own, although some of them are not. Some that Mr. Small has criticised are not what I think at all, but I put them in because the members of the committee gave that as their opinion.

In regard to what he says about rapid cooling, our experience has not been along the lines which he spoke. I think it is probably true that if the solutions are put in water at 19 degrees and cooled right down, more comparative results would be obtained by that method of cooling, but I do not believe that they would agree as well with the method we have now which is also permitted.

MR. REED:—Mr. Chairman, I cannot quite see in regard to the point brought up in the chroming, what particular difference it makes whether all the chrome is absorbed or not as long as we get our results.

MR. ALSOP:—I would say in reference to that that while I have no proof to offer, I do not believe you would always get the same results, at least that has been my experience in what work I have done on that line. If everybody had hide powder exactly the same probably we would get all the same results. If there happened to be some difference I believe it might make a difference between slow and rapid chroming.

MR. REED:—Now, another point, about the determination of the acidity of the hide powder and specifying a method for doing it. Judging from the results that are given in the table of comparative results in determination of acidity, where identical methods were pursued, I do not think we are going to show very close agreement. It would seem needful to have some other method of making the acidity determination. I be-

lieve myself that the fault is entirely in the method, and that the acidity of hide powder was practically uniform. I am not in favor myself of having every analyst himself endeavor to bring the hide powder up to a definite acidity. I am afraid we will get into trouble if we do. I would much rather have the burden put upon the manufacturer of the hide powder for a definite acidity.

Mr. Yocum:—I quite agree with Mr. Reed in reference to that. I think that the limits of acidity of hide powder should be established so that the manufacturer of the hide powder can get within those limits, and then compel him to be within those limits, because the moment you attempt to alter the acidity or alkalinity of a hide powder you are going to ruin it for our purposes. I want to so far as I can back up Mr. Small in his speech. I think he has covered the whole thing, but I do not think he has called to the meeting's attention with sufficient force the fact that it is absolutely essential in the determination of insolubles to have a uniform temperature. It is said here that some of them ran as high as 28 or 30 degrees. Such an analysis cannot be compared with one running at 20°.

Mr. Small:—If we are going to insist upon the manufacturer of the hide powder furnishing us a hide powder with a definite acidity, I would like to inquire how we are going to know whether he does or doesn't do it if we have no method by which we can determine acidity?

Mr. Reed:—That is what it all comes back to, Mr. Chairman. For example, if the various analysts had been told to make their hide powder this time to a definite acidity and we take this table and we run down and see what results we have,——

Mr. Small:—Didn't they? They were so instructed, they were told to use hide powder within certain limits, and if they did not find the hide powder within those limits they failed to obey their instructions if they did not bring the hide powder to the acidity called for.

Mr. Reed:—I don't know about that.

Mr. Oberfell:—Regarding the matter of temperature, Mr. Mosser made a very helpful suggestion in keeping the tempera-

ture at 20 degrees. He suggested the use of a heavy paper bag to slip around the flask, which would eliminate radiation to a great extent and thus help to hold the temperature at 20 degrees.

Regarding the matter of setting the flasks containing the analysis solution in water at 19 degrees; is there any objection to the agitation of this solution?

It took as long as 80 minutes in some cases to cool the solutions, while if they had been agitated it would have taken less time.

MR. SMALL:—The method does not forbid agitation; you may agitate all you choose. The revised method is simply so devised that agitation is not necessary. If you use water at 15 degrees you would be obliged to agitate in order to secure anything like concordant results, but as the method is now defined you may agitate or not as you prefer and still obtain concordant results.

MR. OBERFELL:—You stated that the object of the committee was to get away from that.

MR. SMALL:—The committee felt that a man putting through a bunch of analyses usually has his time fully occupied, and the fewer manipulations he was called upon to perform, the lighter his load, and therefore we would so draw up the method that he would not be obliged to agitate the flask and stand over his cooling device for fifteen minutes or half an hour or what not; but if a man prefers to do so he is at perfect liberty to.

MR. OBERFELL:—That is all right, but if he is going to choose to do that I think he could use a lower temperature and thereby save time again.

MR. SMALL:—That again is where the committee differs with you, at least that is where I differ with you.

MR. OBERFELL:—The difference between the temperature of the water, or 19°, and the temperature to which the solution is to be cooled is so small that it takes a great deal of time——

MR. YOCUM:—But that is exactly the reason, so that you will not get a condition of precipitation due to a wider variation in temperature.

MR. OBERFELL:—But Mr. Alsop on the other hand states that he finds as a result of his experience that considerably lower temperatures can be used.

Mr. Alsop:—I do not advocate using them though.

Mr. Oberfell:—If there is no difference, why don't you advocate them?

Mr. Alsop:—Because we have not got all the chemists standarized.

Mr. Oberfell:—In 1910 I was chairman of the committee for the rapid chroming of hide powder, I had the committee do some work on the actual estimation of the amount of chromium absorbed by the hide powder, both by the rapid and slow cooling, and while I am sorry that report is not here, my recollection is that there was essentially no difference in the absorption of chromium by the hide powder by the 24 hour method and the 1 hour method by shaking; that was by actual estimation of the chromium in the hide powder.

Mr. Faust:—I believe that the weakest point in the entire method at present is in the insoluble determinations, especially in the case of ordinary quebrachos or hemlock extracts, and while the committee has limited the temperature down to 20 degrees, and it is very easily possible to keep the temperature of the solution in the flask at 20 degrees, it seems to me that the trouble is in the solution that is on the filter paper. Now you cannot keep that solution down to 20 degrees unless you use some sort of a jacket with running water, and the great differences in insolubles in ordinary quebrachos would be partly eliminated by such a method.

Mr. Loveland:—Don't the members of the committee think the filter paper has a great deal to do with that as well as the cooling of the solutions? I have "590" papers in my laboratory that vary a great deal in thickness, and in a number of packs I have to throw out from fifteen to twenty filter papers in every hundred, and I think if I should use those thick and thin filter papers on duplicate analyses my results would vary a great deal more than difference of temperature would cause. And another thing I think, although Mr. Oberfell says the same amount of chromium is absorbed by the one hour or the twenty-four hour chroming, that the hide powder has to me a different structure, a different feeling, with the rapid. I get a fluffier hide powder, and I believe the difference in the analysis on rapid and

slow chroming on solid extracts is due to that very fact, that one forms a mat while the other is a fluffy hide powder and allows the tannin in there to become absorbed on account of the high non-tans of that extract.

MR. YOCUM:—I hardly think, Mr. Loveland, that your statement as to the effect of temperature should be made so broad, because the temperatures undoubtedly have a decided effect on insolubles, and a solution at 150° F. will be clear when at 70° F. it will be cloudy. Now by reasoning that out, a limitation on temperature is absolutely essential. What you say about filter paper is absolutely correct, but notwithstanding that, we endeavor to overcome the absorbent power of the paper by running through a quantity of tannin solution before collecting for analysis.

MR. FAUST:—The average chemist sorts out his filter papers, takes out the unusual ones and tries to get them as uniform as possible, and I think the greater part of the differences are caused by differences in temperature.

MR. NORRIS:—Looking over this table, I should not think that was so. If you look over the time of filtrations there are some as low as 50 minutes for quebracho extracts; there are others over 3 hours. Now how do you account for that? I think it is largely the filter paper, and I have some filter papers here with me. I would just like to send them around and let you look at them yourselves. I think Mr. Loveland is right in what he says. I have found as much as 40 per cent. of the filter papers in a pack which were entirely unsuitable for filtration. And I believe the temperature is also another chief difficulty there. For instance, if you take a sample of extract,—say the extract is analyzed in Laboratory A, on a day that the laboratory temperature is 20 degrees, they are not going to get the same results as B laboratory, probably analyzing two or three days later with 28 degrees. I have found those differences myself where I tried to duplicate a quebracho extract where I had 20 or 22 degrees one day and 28 degrees the next. I cannot do it at all.

MR. YOCUM:—The point is that the temperature is something

that is capable of being regulated, and is it possible to regulate filter paper?

Mr. Norris:—Yes; a careful selection of your paper will obviate a lot of that difficulty; but I would recommend getting away from the filter paper entirely for those tanning materials in which there is a large percentage of insolubles. I would recommend trying the Berkfeld candle again, or some such method as that, so that we can shorten the time of filtration. We tried out the candle about seven or eight years ago and we did not find it satisfactory, but, as I understand, that candle has been much improved and it is being used quite successfully in the International Association to-day, and I do not see why we should not try that out again, or some similar method for the insolubles.

Mr. Faust:—The secretary of the Association might write to Schleicher and Schull and ask whether it would be possible for them to make for the Association a filter paper of more uniform thickness.

Mr. Reed:—I was going to suggest something of the kind myself. Not only that, but I do not know whether any of you have gotten any filter papers within the last three weeks. I have, and if I am not mistaken we are going to be up against the same old difficulty we had some years ago. The papers I have received last are so absolutely rotten that you cannot fold them without breaking.

Mr. Yocum:—We have been getting that right along.

Mr. Reed:—I have been having pretty good papers, but the last that came in were absolutely rotten.

Mr. Veitch:—I want to remind the association of one thing here, that you are talking about mighty good results, all of them.

Mr. Yocum:—You should have been here yesterday afternoon.

Mr. Veitch:—Whatever may have been the variations you have here, they are evidently pretty small. These are all good results, I think. Don't let us split too many hairs.

Mr. Yocum:—Mr. Delaney yesterday objected to 3 per cent. on the total difference.

Mr. Alsop:—I do not think it is worth while to talk much longer about filter papers. We have to use them. It might illustrate to Mr. Delaney why chemists cannot get exactly the same on an extract. We have to do the best we can.

With reference to the acidity of hide powder, I think that that determination is more a matter of experience than anything else. If a man is used to doing it he can get good results by either Mr. Small's method or Hough's method or the one we use. I think it is more inexperience than anything else that has led to the large differences in this report.

Mr. Small:—I think we are all willing to admit that the filter papers do vary, and I think the suggestion that was made a few minutes ago is the successful solution of the problem, namely, that we instruct the secretary to explain to Messrs. Schleicher and Schull the difficulties which the Association encounters, and ascertain whether they can and will manufacture or sort out for the Association papers of a certain definite thickness or weight. In order to bring the thing to a head, I would move you that our secretary be instructed to take this matter up with Messrs. Schleicher and Schull as suggested.

(Motion seconded and carried.)

Mr. Veitch:—I will say this about the filter paper: It is not only a question of thickness or only a question of weight; it is the two together. That is, you may have a thick paper that is very porous and open formation, and you may have a thin one that is very close formation, and the thick paper would be the more rapid filter decidedly. You have to take the two things together. You have to get a paper within definite limits of thickness and definite weight.

Mr. Smoot:—I would suggest, make that "uniform" paper instead of "definite thickness." Say "more uniform paper;" because as you say sometimes the paper is thicker in spots. To make it a more uniform paper is what we are after, not so much a definite weight paper.

Mr. Veitch:—The Secretary will take care of that, and ask for a paper of uniform weight and thickness.

Mr. Yocum:—Mr. Reed says they break. Now that is due possibly to the fact that the acid has not been properly washed out of it, which will have an influence in the result.

Mr. Norris:—Aren't the ones which break usually the soft, thin ones?

Mr. Reed:—Not at all.

Mr. Veitch:—They are the hard ones.

Mr. Reed:—No, they are not; they are the soft ones.

Mr. Alsop:—If there is nothing more to be said on this, I would like to say that I do not want the impression conveyed to this meeting that these analyses here are a poor lot, because I do not think they are. Where a lot of collaborators work on samples like this, in my experience there are always a few who differ considerably from the majority, and that was the case here. A great majority of these analyses were very close, I think, when you consider the extracts that were analyzed.

Mr. Hurt:—I do not agree with Mr. Alsop about that. If he excludes all of the analysts who differed and then compares the ones who are together, why, it looks very good, but it bears out just what I said yesterday. It seems to me where two or three are different and the two or three are operating laboratories, if we are going to have that difference we should try to get still closer than we are; and when they are 3 per cent. off or 4 per cent. off, it seems to me unfair to exclude the ones that are low and then say we are all right.

Mr. Alsop:—I did not say all; I said a few.

Mr. Hurt:—I mean the few that ran low.

Mr. Alsop:—And the fact that there are only a few I think shows conclusively that it is their fault and not the fault of the method.

Mr. Smoot:—Before we get away from this, I would like to say in regard to that question of hide powder, that I do not believe the time is long enough for the rapid chroming, and I especially found it true of ordinary quebracho, and I found it true in the committee work. I did not get as good results by rapid chroming where ordinary quebrachos were used as I did by slow chroming, and I believe if the time were longer I would get them.

MR. REED:—I would like, Mr. Chairman, before we leave the methods—this is not perhaps exactly pertinent, and in one way is—I want to bring up a question on the methods of sampling. I would like to have an opinion from the Association. The question has been raised when a shipment of a large number of bags of a material coming into this country, say 40,000 bags of extract, is sampled according to the official method method, the one per cent. of the shipment sampled, and representing the cargo, also represents smaller lots. If carload lots are furnished a tanner, does the Association understand that the one per cent. sample representing the entire cargo, also represents the single carload shipment from that lot?

MR. YOCUM:—Mr. Reed, if you will permit me, I have had something along that line come up several times in the last year, and acting for the tanner I have consistently advised that the tanner draw his sample from the material that was shipped to him, and that the sample drawn from a 40,000 bag lot where the tanner receives but 10,000 of those bags is not fair to the tanner, and it is something that the tanners ought to take up and consider, that the sample should be drawn at the time that the material is weighed, and from the material that is to be delivered to him. I cannot say anything further than that. That is my position about it. The facts are that the method is a little deficient. It says, "When carload lots of 400 bags or less are to be sampled, 7 per cent. of the number of bags shall be sampled." It is only 1 per cent. when it gets up into a thousand or more. Isn't that correct?

MR. SMALL:—Mr. President, as one of the committee that drew up this method of sampling, I would like to say that I think it was the intention of the committee that the directions for sampling should be applied to the lot which constituted the transaction, that is, if a manufacturer sells a lot of extract to a broker, the number of bags involved in the transaction is the unit to be sampled. If, however, a portion of the above lot is sold by the broker to a tanner, an entirely separate business transaction is involved, and the quantity of extract involved in this second transaction is the unit to be sampled according to the method of the Association. What might have happened in

the transaction between the extract manufacturer and the broker is of absolutely no concern as far as the second transaction is concerned, which is an absolutely independent transaction which involves an entirely separate sampling to represent the material that is bought and sold.

MR. YOCUM:—Just let me read what it says: "When carload lots, or less, of bags are to be sampled, 7 per cent. of the number of bags shall be sampled. When shipments of more than a carload and less than 2,000 bags are to be sampled, 20 bags shall be sampled. When shipments of more than 2,000 bags are to be sampled, one per cent. of the number of bags shall be sampled." Now generally speaking, that relates to incoming shipments, because as a rule the outgoing shipment from a point of receipt is in carloads.

MR. REED:—Yes.

MR YOCUM:—And if you were to attempt to sample 7 per cent. of every carload that was shipped to a buyer, you would be in trouble right off the job; but as a matter of fact what is tangible and available is that when a shipment is loaded on a barge for trans-shipment, particularly in New York, the sampling of that lot as it goes on and as it has been weighed is perfectly feasible and a proper place and time to do it. The method should be a little more specific in reference to the sampling, I think.

MR. HALEY:—Does not the present method of sampling as outlined provide really two methods of sampling, one covering the material that is imported into this country, and the other covering the material that is manufactured in this country? The original idea of sampling one per cent. of the total number of packages was to cover the sampling of large cargoes of imported material; that was a transaction between the foreign shipper of the merchandise and the American buyer, the American buyer taking the entire cargo. The unit to the American purchaser under those conditions was the entire cargo, and consequently it came under the strict interpretation of sampling rules that it be sampled for one per cent. When, however, the American purchaser became the seller of that product, different methods of sampling were required, for if he split up the cargo—as was

generally done—into units of carloads, he should be required to comply with the method of sampling and sample each carload as a carload or 7 per cent. of the number of bags contained in a car. Every domestic manufacturer or seller of extracts presents with his invoice to the buyer an analyses representing the individual car that the buyer receives, and as I understand this discussion, it is to ask an importer whether or not in the purchase of an individual car of an imported extract the purchaser receives an individual analysis of the car that he purchases in accordance with the method prescribed by this association for sampling, or does he receive an analysis representing one per cent. of the entire shipment as it arrives in the port of discharge?

MR. FAUST:—I believe we should take the method as it stands and put in an amendment like this: "A sample drawn from any shipment of extract should not be considered as a sample of any subdivision of the shipment," or something to that effect. I believe if we made this an amendment to the first paragraph, it would cover this entire matter. I do not believe it is a weakness in the method, but only a case of not following the method.

MR. SMALL:—We have at the head of the methods of sampling some general remarks. If it seems desirable I would suggest that there be included in the general remarks a paragraph embodying Mr. Faust's suggestion, if he wishes to draw up something and present it to be acted upon.

MR. YOCUM:—I certainly do think that it is essential to have it understood by the tanner that the sample of his purchase, whether it be a carload or ten carloads, that the sample of which the analysis is made should be of his purchase and not of a general conglomeration.

MR. VEITCH:—It seems to me it is a matter entirely without the jurisdiction of this Association. If the purchaser of any lot of material is willing to accept any old analysis that is given him without indicating what it applies to, that is his lookout.

MR. YOCUM:—It may be true that it ought not to be brought up here, but we are the fellows that have to do the sampling. It may be the National Association would be the ones to bring it up.

MR. VEITCH:—We do not do it except on the request of the purchaser or seller, and you do it for that particular lot.

MR. YOCUM:—We do it on the request, but we get the blame. If when the tanners receive the goods they do not agree with the analysis that has been forwarded with them, and that not being our fault, we kind of object to it.

MR. REED:—The criticism has been directed at an official method of sampling of this Association, that is, against, you might say, the clarity, the clearness, of the wording of the official method. It seems to me that in that respect it is up to us.

MR. WALLIN:—I agree with what Mr. Reed has said and also with what Mr. Small has said. I think the tanner looks to this Association to say how that sample should be drawn, and if he does agree to abide by the rules of the A. L. C. A., and that sample can be drawn for a whole cargo and he would only get one or two loads of the cargo he would be bound by it. That would be manifestly wrong, and if there is any way in which that could be cleared up I think it would be in order to make the change which has been suggested by Mr. Faust. We want a sample drawn from the purchase that we buy.

MR. VEITCH:—All you have got to do is to specify it.

MR. WALLIN:—I doubt it. At least, it seems to me that the method of sampling should state so. This present official method of sampling might indicate to the broker, for instance, that he did not have to sample from the carload but that I would have to take under the A. L. C. A. method, the sample of the cargo of which that was a part, and probably I would have to take it.

MR. YOCUM:—And certainly the method is not clear on that point.

MR. TEAS:—I think the method is only meant to cover the physical means of taking the sample, not to prescribe any restrictions on the buyer and seller. That is a matter between the buyer and seller.

MR. VEITCH:—That was my view of it.

On motion, the matter was referred to the Council for action.

COMPARATIVE EXTRACT ANALYSIS.[1]

By Charles R. Delaney.

At the annual convention of the American Leather Chemical Association held in Washington last year you may recall that there was some discussion concerning the advisability of fitting up a small laboratory wherein the various gentlemen who are held in repute as the final arbiters of extract analysis could see each other go through the usual analysis, to the end that there could be found a closer agreement between them when it came to the final figures on which many hundreds of thousands of dollars worth of extract is sold. Notwithstanding that in numerous other industries greater concordance has been found by the getting together of the chemists and thrashing out the smaller details making far greater accuracy in the work, notwithstanding this there was a considerable objection raised and the matter was dropped in so far as surface indications showed.

But the fact remained that when samples were drawn of a given shipment of extract that there would often appear a difference between the findings of different operators which often worked hardships to either the manufacturers or the customers. It might be said that in the law of chance there would be a probability of errors neutralizing themselves in the course of time, but it can also be said that with an exact method, the errors should be constant and not variable.

As manufacturers of myrobalan and sumac extracts for the tanning trade, which as you well know command a high unit tanning cost, we found that the only safe thing for us to do to avoid trouble, was to deliver extracts considerably beyond the minimum guarantee whenever we were called upon to ship extract of a certain total solid content or available tannin percentage or in other words we would have to ship say 105 per cent. of what we guaranteed if we wished to be absolutely certain that our materials would conform to a certain standard when tested by the various recognized laboratories of the trade.

As our business in the last two years has been increasing, and the cost of raw materials advancing at a still greater rate, we

[1] Read at the Ninth Annual Meeting of the *A. L. C. A.*, Washington, D. C., December 5, 1912.

decided some months ago to send out certain samples of a standard myrobalan extract in order to find out two things, namely, whether the difference between analysts was caused by an inexact method—which would be shown by the difference in results of one operator working on two samples of the same extract—or whether it was caused by the little manipulative differences which crop up in every analyst through some small differences in the way work is handled, apparatus tested and so on, this being of course shown by differences in results of the various laboratories, yet with agreement among themselves; and I am glad to say that it is our experience that this latter is the case—which is precisely the reason why the matter was brought to your attention last year.

In order to find out what we wanted to know we made up ten cars of extract sending out two samples of the first lots and carefully checking in our laboratory on the eighth car, we waited until half of the batch had been tapped out, while being constantly stirred and then we drew a large sample from the extract as it ran out, took it to the laboratory and stirred it for fifteen minutes very thoroughly, then quickly filled twelve bottles holding about four ounces each, stoppering them tight, and to insure additional precaution they were filled in this order 1-4-7-10-2-5-8-11-3-6-9-12. Then we took the first four and marked them car No. 8 and the second four marking them car No. 9 and sent the 9th sample to a private laboratory and kept the other three. The results for which we paid $3 per test were as follows:—

	Laboratory A		Laboratory B		Laboratory C		Laboratory D	
Gravity	53.2	53.0	54.0	—	52.7	52.8	53.8	53.8
Total solids	49.60	49.30	50.28	—	50.24	50.21	50.22	50.42
Soluble solids	46.86	47.07	48.52	—	48.36	47.74	47.54	47.74
Insoluble solids	2.74	2.23	1.76	—	1.88	2.47	2.68	2.68
Non-tannins	17.22	17.46	17.75	—	18.45	18 23	18.08	18.13
Av. tannin	29.64	29.61	30.77	—	29.91	29.51	29.46	29.61

Taking these as they stand they differ as follows:—

	Degrees		Per cent.
Gravity	52.7 to 54.0	Tw. or	2.47
Total solids	49.30 to 50.42	"	2.26
Soluble solids	46.86 to 48.52	"	3.54
Insoluble solids	1.76 to 2.74	"	55.68
Non-tannin	17.22 to 18.45	"	7.14
Tannin	29.46 to 30.77	"	3.32

With such a showing as this it is obvious that to make a price

on his product which will return a just amount of profit, the manufacturer must necessarily specify *one* particular laboratory as the arbiter of value of his extract, and yet this is not right. If you say that three of the laboratories showed concordant results on the available tannin, kindly look at the figures for the total solids, in one case 49.3 in the other 50.4—yet it is usually conceded that a total solid determination is by no means more difficult to make than a non-tannin estimation. For the sake of stating the matter precisely, let us suppose we had agreed to ship 50 cars of extract to meet a basis of 50 per cent. total solids at a cost of 5 cents per unit and our friends specified laboratory A when we were checking by laboratory D, our net loss would be $843.75 or if the tanning unit were specified at let us say 9 cents and we agreed to sell upon D's certificate and were checking by B, our net loss would be $1250.00. The whole idea of buying and selling on a basis of tannin depends upon the exactness of the analyses and the constancy of the errors, and now when we do have a method that is good for the purpose it is intended for, please let us check up our little errors of manipulation that have crept in, standardize our flasks, check up our weights, and see that one man doesn't drain a 100 cc. pipette for two minutes and another operator not at all.

We as extract makers are not to be in size nor output compared to some of you here but we feel that it is not right nor just that we should be compelled to pocket avoidable losses when competition is so keen that profits are reduced to the absolute minimum, and I therefore take the liberty of emphatically seconding the suggestion made a year ago that either at or before our next convention, a small laboratory be fitted up and the various public experts check together where they can see how the other works in order to insure that they at least make their errors consant.

DISCUSSION.

Mr. Yocum called attention to the fact that the concordance in results of tannin analyses is as good as is found in other commercial analyses. He expressed the opinion that inaccuracies in instruments are not responsible for much of the difference found.

Mr. Reed read an article from the JOURNAL for August, 1912, on extract analysis, showing very good agreement among three laboratories.

Mr. Teas said that results on chestnut extract were nearly always satisfactory, agreeing much better than analyses of some other organic materials, and quite as well as some inorganic ones. He thought that Mr. Delaney's difficulties were due to the fact that the extracts in question are more troublesome to manage than most, and that chemists in general are less familiar with them.

Mr. Delaney said that in the licorice paste industry difficulties due to failure of different chemists to agree were solved by all the chemists who were working at the material getting together and working over the method together.

Mr. Hurt called attention to the necessity of having the bottoms of drying ovens level, so that the thickness of the film of material may be uniform.

HOW LONG SHOULD CHESTNUT-OAK BARK BE STORED BEFORE LEACHING?[1]

By Charles C. Smoot, 3rd.

I realize that the number of factors to be considered in arriving at an answer to this question are numerous, and that most of them are beyond the control of the average tanner, or the man in charge of the works. But, taking the promise, that the tanner can have his choice of equally well cared for bark, peeled in the same locality, one pile being six to nine months from the tree, and the other thirty to thirty-six months from the tree, which would he take to grind? This narrows the question down to one of quantity and quality of yield, and it is along this line that I want to attempt to answer this question.

You will find in the literature published in many places, the statement that bark loses strength on prolonged storing, and some writers even go so far as to give tables, showing the amount of loss sustained by different qualities of bark, stored for certain

[1] Read at the Ninth Annual Meeting of the *A. L. C. A.*, Washington, D. C., December 5, 1912.

periods of time. But nowhere have I been able to find anything bearing on the quantity of a certain specific gravity liquor it was possible to obtain from a known amount of absolutely dry bark of different ages. Nor, is there, that I can find, any statement showing the difference, if any, in the quality (meaning by quality, the different percentage of tannin to non-tannin, in the liquors obtained).

I have often asked old tanners the question: "Which bark, old or new, gives you the best results?" The invariable answer has been: "New bark gives the most liquor, and I believe, the better gains." Now, to prove or disprove this answer the following series of tests were made:

Two piles of bark, of as nearly as possible equal quality, and coming from the same locality, were selected. Each lot contained about 3,000,000 pounds, the only difference being in the length of time they had been on hand. One pile had been peeled in the spring of the year in which the test was made; so was from six to nine months old at the most. And the other lot had been peeled two seasons previously and was, therefore, from thirty to thirty-three months old.

The bark was ground and leached under, as nearly as practicable, the same conditions, and the records show that they were remarkably uniform. Each leach of bark was sampled as ground and cast. The liquors obtained from each leach were also sampled, and a record of the number of cubic feet obtained was kept. Each week composite samples were taken and analyzed, the results calculated to a uniform basis, and the average taken. They show the following:

	Cubic feet of 40° barkometer liquor obtained from 100 lbs. of absolutely dry bark	Per cent. of non-tannin in 40° barkometer liquor
Six to nine months	3.31	5.20
Thirty to thirty-three months	3.16	5.10

	Per cent. of soluble tannin in a 40° barkometer liquor	Per cent. of tannin to 1° barkometer
Six to nine months	5.41	0.135
Thirty to thirty-three months	5.53	0.138

	Per cent. total solids which was tannin, or purity
Six to nine months	50.0
Thirty to thirty-three months	50.7

To show how near alike these barks were treated, I submit the following, showing in each case the difference between the amount of tannin found in the fresh sample and the amount remaining in the spent sample.

Six to nine months	10.73%
Thirty to thirty-three months....	10.52%

The amount of tannin obtained in yard liquors was within 2 per cent. of the amount shown as available in the bark, under this system of leaching.

Now what do these results show, in answer to our question to the old tanner? They certainly show that he was right as to obtaining more liquor from the new bark; but what about more weight? I think that the old tanner would certainly have said nice things about his barkometer, if this had been his only guide. For the quality of the 40° liquor is certainly much lower than it would have been if his liquor had been made from older bark. Of course this would affect the weight, provided he kept all other factors the same. Therefore, our old friend would be much more apt to make poorer, rather than better, gains, which he anticipated.

Summing up what these figures show, we have:

1st: New bark produces more liquor, but of a poorer quality.

2nd: The amount of actual tannin obtained is practically the same from both kinds of bark. Showing that there is no appreciable loss of tannin caused by age, up to the time limit of this test.

3rd: That there is a difference in the solubility of the tannin in old and new bark. That in old bark being more easily soluble gives the better quality liquor.

Therefore, when the cost factor does not prevent, bark should not be ground until thoroughly aged; this time being different for different localities.

REPORT OF COMMITTEE ON COLOR TESTS.[1]

By H. C. Reed.

We used in these tests the cow grain split, the sheep skiver and what we might call an under-grain split, that is a cow grain split with the grain buffed off, and the result of the work will be found here if any one wishes to look at them. They are very unsatisfactory.

The directions were as follows:

1. Lay away in a ½ per cent. tan solution for 2 hours and then in a 6 per cent. tan solution for 40 hours. Wash in distilled water with repeated squeezings to remove as much excess tan liquor as possible and shake for 15 minutes in distilled water, remove and shake another 15 minutes in fresh distilled water, slick and tack on board, placing in dark, cool place to dry. Oil ½ of test.

2. Lay away in a ½ per cent. tan solution for 1 hour, then in a 1 per cent. tan solution for 3 hours, then in a 2 per cent. tan solution for 4 hours and finally in a 6 per cent. tan solution for 33 hours. Wash, dry and oil as in (1).

3. Lay away in ½ per cent. tan solution for 2 hours and then in a 3 per cent. tan solution for 40 hours. Squeeze and oil as in (1).

4. Tan by shaking ½ hour in a ½ per cent. tan solution and for 6 hours in a 3 per cent. tan solution. Remove and lay away over night in a fresh 6 per cent. tan solution. Squeeze and oil as in (1).

5. Tan by shaking ½ hour in a ½ per cent. tan solution and for 6 hours in a 3 per cent. tan solution. Remove and lay away over night in a fresh 3 per cent. tan solution. Squeeze, wash and oil as in (1).

NOTE: All skins to be approximately 3 in. by 2 in. and tan solutions employed to be in each instance 200 cc. in volume.

The result of the work seems to prove, what we practically knew beforehand,—it is almost impossible to get any sort of uniformity from different skins. One skin especially that was sent out by the chairman is entirely unfit for use. If I had examined it before sending it out I would not have sent it. On the whole I am inclined to think from the results that there

[1] Ninth Annual Meeting, A. L. C. A., Washington, Dec. 7, 1912.

may be something gotten from the undergrain split. I think the results seem to prove that there is greater uniformity with the use of it than there is from the grain, but so far as the sheepskin and the cow grain splits go, there is a decided lack of uniformity. I would like to have you look at these and see. I myself think that to get any sort of results on the color valuation of tanning materials we will have to get away from this method of testing, possibly to a tintometer method, or along similar lines. I would like to have the Association take up the method of impregnating cloth with gelatine,—animalized cloth. Something that I tried out rather hastily was the impregnating of paper with gelatine. A test seemed to indicate that one could get a pretty fair indication of the color of a tanning material by impregnating paper like blotting paper, with gelatine. At any rate it gives a test that I think approximates leather in its appearance.

MR. VEITCH:—Is it a deeper color than cloth?

MR. REED:—I think if anything it is deeper color than cloth, decidedly deeper than the old provisional method that we had; but the entire matter must be taken up and worked out because we do need some kind of method that will give comparable results. I might read the comments of the collaborators. Mr. Oberfell says: "This is the first time I have worked cow grains or skivers and I think the grain gives a better indication of what the tanner may expect than sheep skivers; whether or not the cow grains will indicate slight differences in shade is a question this work cannot bring out. I do not consider the cow splits worthy of comment. As to the procedures it is my opinion that nothing is gained either by laying-away, tanning in graded liquors or using such strong liquors as those containing 6 per cent. tannin. It would be quite impossible in most cases to have sufficiently large samples to use the 6 per cent. solutions. I think just as good if not better tests are obtained by tanning in a 2 per cent. tannin solution for 24 hours by intermittent shaking, using 400-500 cc. of liquor and non-tannin machines for the agitation. The full effect of the color value is obtained by this procedure.

"I am as yet undecided as to the merits of oiling the test pieces. Care and a very light oiling are necessary when using

sheep skivers or cow splits to avoid oil stains. In case it is decided to oil the tests I would advise that you change the wording of your methods by directing the oiling before drying. Anyone not familiar with finishing leather would from your directions dry and then oil which would always produce oil stains and is not the procedure followed by tanners.

"In depickling sheep skivers I am much in favor of a 'sour bran drench' in place of a solution of formic or acetic acids. The 'drench' clears the grain where other methods do not and the acidity of the drench is always correct to give the skins the proper plumpness. I have found that the thicker a sheep skiver the darker the color test, so that the drench insures a uniform plumpness by different manipulators. I never have favored the use of the dry pickled skivers and think I get more uniform tests from the moist pickled skins."

The directions given were for the preparation of the sheep skivers. They were sent in the pickled condition, whereas the cow grain splits and the under-grain splits were sent already prepared for use, preserved in borophenol.

Mr. Small says: "I am sorry, but in several respects the samples are a better illustration of poor technique than of the merits or demerits of any particular method of making color tests. In particular the first set of sheep skin skivers received (marked A) were either from a damaged skin or suffered in the preliminary wetting-back stages in this laboratory, for they presented a warty appearance throughout. Some of the grain splits were insufficiently washed and insufficiently oiled before drying.

"Despite these shortcomings certain facts seem to me to be established by these samples. First,—that a certain amount of variation is to be expected from the use of different splits or skins;—that this may be lessened by suitable treatment but will probably always be somewhat in evidence. Second,—that as between the several methods of tanning tested there is no essential difference in result produced.

"Further study of the preliminary preparation of the split or skin and of the washing and drying operations should lead to a satisfactory working method."

DISCUSSION.

MR. FAUST:—Mr. Philip Armstrong suggested a method some time ago which might be worth considering. We tried it out in our laboratory, and while the results do not indicate anything conclusive, I believe it should be tried out thoroughly by next year's Committee. In this method skins are dehydrated with alcohol. I have some tests here made in this manner. They do not agree very closely with the tests we make according to our present method. We also tried dehydrating with Glauber salts, and I also understand that potassium chlorate would be satisfactory. We put the skins in a saturated solution of Glauber salts, and then in the alcohol, leaving them a couple of days, and then using them for color tests, and as far as we went, the method, with a few modifications perhaps, looks very promising.

MR. LOVELAND:—I would like to ask Mr. Faust, in the use of Glauber salt and alcohol, whether he gets a lighter colored test than by the ordinary method. I have found that by the addition of any salt, sodium chloride or magnesium sulphate,—I never tried Glauber salts,—to my solution of tan liquor I produced a lighter colored skin with a softer feel than with the ordinary method, and it was my idea that by saturating the pieces with Glauber salts and then putting them in alcohol, the sulphates would be precipitated in the skin and you would get a lighter color.

MR. FAUST:—There was some action, because those skins came out the lightest. You would get more indicative results with alcohol alone.

MR. LOVELAND:—I have used those salts and I got the spots due to the presence of iron in the salt, and it was always a lighter colored skin in general, except the spots.

MR. FAUST:—The reason I thought this would be a good idea was, that if the alcohol method could be worked out, we could get our skins from a central source, a certain member of the Association could furnish us with the skins and they could be prepared and sent out in alcohol to the various members.

MR. VEITCH:—Mr. Small, have you anything to say?

Mr. Small:—I do not know that I have anything special to add to the comments that I made on the Committee report. I do think, as I said there, that the evidence from these tests goes to show that the particular method of tanning the skiver is immaterial. I should judge from the evidence that it makes no difference whether you use the 3 per cent. solution or the 6 per cent. It makes no difference whether you put your skins right into a 3 per cent. solution to start with or first in a quarter, then a half, then a one, then a two, and so on. That seems to be the result shown by the tests that I put through.

Another thing, from the evidence I should say that it would be impossible to secure absolute uniformity by having any central source of supply of the skins, unless somebody cut up a large number of skins and made color tests with samples from them and then collected the particular skins that happened to give the same grade of color, and I am afraid that is not a feasible proposition. Take, for instance, the grain splits which I prepared for the Committee. They were all handled in essentially the same way, and yet they do show a certain amount of variation in the ultimate color produced. I do believe that there never will be for general usefulness anything found to take the place of a piece of hide. I think that the tanners, the practical men, are interested in having a piece of leather to look at and feel of, from which to form their idea of the color value, and some of them seem to think that they can get some idea as to the quality of the leather that they may expect from these color tests, and that being the case, though we may have a standard method and may find it desirable to use animalized cotton or something of that sort, I doubt very much if we ever will be able to avoid entirely the use of grain splits or sheep skin skivers or something of that sort. I think a great deal of the variation in results may be ascribed to the technique of the process. Any one who has been accustomed to the use of sheep skin skivers and then switches over to the use of grain splits will in all probability produce some rather wonderful results for a while until he becomes used to the method of handling them. The washing process after tanning is particularly important, and as far as the oiling is concerned the idea is the

same as in the tannery, to prevent the action of the air on the skiver during drying. In the case of the sheep skins the skins are sufficiently oily so that the oiling apparently makes practically no difference. Many samples show no difference whatever between the oiled half and the other half, but in the case of grain splits the difference is quite marked; and in my experience where oil is used, you are able to get a series of color tests with colors much more alike than you can where the oil is not used. As I say, I doubt very much if we can ever avoid entirely the use of something of this sort, and I think it is desirable to keep pegging away at this thing in order to get a method which will give the best results possible, although I don't believe that we ever will be able to get a method which will give results that will always be the same.

MR. BALDERSTON:—It might be possible to combine these two things. If an extract maker wishes to know how the color is running, if he had a set of color tests made on some standard kind of animalized cotton or paper he would have then a comparison of the several lots, and if he had along with those a test made on a grain split, he would know what the other characteristics were.

MR. REED:—One can get, it seems to me, a pretty good idea of the color of the material and get uniform results by the use of hide powder, but it is open to the objection raised by Mr. Small that as an exhibit to a tanner it is very nearly worthless; there is no way of putting it in a form to properly exhibit it; but one can in the laboratory get a pretty good idea and duplicate his results by this method, and we have there a standard.

MR. EVANS:—I have done some work on color testing, using the method that was abstracted in the JOURNAL some months ago of taking chrome tanned stock. In liquid extracts, take about 25 grams and dissolve it in 100 cc. of water at 70 degrees, and let it cool, and then place the chrome leather in it in the shaker and shake it for one hour and let it stand three hours in the dark, and then take it out, wash and dry. The blue or green color of the chrome does not appear to affect the color due to the extract. I think a great deal of the trouble in color tests is due to the fact that you run them with distilled water. There

are no two tanneries in which the water is alike, and the only way for a tanner to tell how his extract is going to work is to run the color test on the water that he uses in his own tannery. It makes quite a difference.

Mr. Veitch:—I don't see, myself, how this animalized cotton or paper is going to be much superior, if any, to the use of wool cloth. I think it was suggested by Mr. Hurt a couple of years ago. We tried it once. Now if some scheme could be gotten by which that color were deepened on the wool cloth, I believe it would pretty nearly be what we are looking for.

Mr. Loveland:—I would like to say as to that wool cloth, that I find it a very good color indication in some cases, but there are some extracts made that will give an absolutely different color on a sheepskin skiver from that which they give on a wool cloth. For instance, if an extract contains an aniline dye you will find an entirely different looking color on cloth from that given with a sheepskin color test.

DEPARTMENT OF LEATHER INDUSTRIES—UNIVERSITY OF LEEDS.

We have received the Annual Report of the Department for the session of 1911-12. The number of students in the day classes was 19, and in the evening classes 20. Two students received the degree of B. Sc. and three others passed the Diploma Examination of the Department. The courses given include under Leather Manufacture, Principles, Chemistry and Physics, Methods and Analytical Chemistry. Beside these, courses were given in bacteriology and microscopy. The Report includes a list of articles published during the year, most of which have appeared in this Journal.

Mr. R. Arnold Seymour-Jones has resigned from the position of Research Assistant to enter commercial work. His place has been taken by Mr. Wm. R. Atkin, and the work on the action of acids and salts on gelatin which had been carried on by Professor Procter and Mr. Jones is being continued with the assistance of Mr. Atkin.

BOOK NOTICES.

LEDERFARBEREI UND LEDERZURICHTUNG. M. C. Lamb.

A German translation by Dr. Ludwig Jablonski of "Leather Dressing, including Dyeing, Staining and Finishing," provided with numerous dyed samples. Julius Springer Berlin, 22.50 M.

MODERNE GERBMETHODEN. Josef Jettmar. A. Hartleben's Verlag, Vienna. 6.30 M.

"Principally a reference book for the information of the non-professional reader, although containing much of use to the specialist." (Rundschau.)

HANDBUCH DER CHROMGERBUNG. Josef Jettmar. 20.50 M.

A comprehensive and indispensable handbook for all tanners and leather factories, treating of all forms of chrome leather, combination processes, etc. . . . a good guide for the tanner unpracticed in this branch . . . numerous illustrations, leather samples, etc. (Rundschau.)

W. J. K.

ABSTRACTS.

Chrome Belting. PIERRE GEURTEN. *Ledertechn. Rundschau,* **1912,** 265-6. Only first class hides can be used; salted hides are softened 2 days in 2 fresh waters daily; liming in straight lime 6 to 8 days according to weight. Java buffalo is soaked the first day in used water, then milled, soaked a day in fresh water, next day milled and entered in a lime containing 2 kg. sod. sulphide for 100 kg. dry hide; 1 kg. suffices to strengthen for a new lot. Liming is complete in 4 days. After unhairing, the hides are cropped and the croupons milled 1-2 hours in water containing 1 per cent. butyric acid reckoned on white weight and are next drummed 4-5 hours at 20° C. in a concentrated pickle containing 3 per cent. alum, 2 of HCl. The chrome extract containing 12½ per cent. chrome alum (white weight = 100) to which has been added 17½ per cent. (alum = 100) calcined soda previously dissolved. This extract is added diluted with an equal quantity of water, 1 pailful hourly while the drum is in motion, the second day every 2 hours. In 3 to 3½ days the tannage is complete as shown by cut and boiling test. After draining a day the leather stays for 3 hours in a 20° Bé. antichlor solution or is drummed an hour with 2½ per cent. antichlor (white wt. = 100). For bleaching, the leather is drummed ½ hour with 10 per cent. $BaCl_2$ and a little water and after washing, deacidified with 1½ per cent. borax. For currying, the slightly moist leather is milled in an air heated drum with 10-15 per cent. (dry weight = 100) of a mixture equal parts stearin and paraffin

or with stearin substitute of the Vacuum Oil Co. The hot air is shut off and 2 pailfuls cold water added with ½ liter benzin per croupon; this is drummed in, then next 2 pails water and ½ k. talc per croupon. The leather is dried in frames and powdered with talc giving a product equal to the best double bath ware. W. J. K.

Annual Report of the Vienna Versuchsanstalt and Gerberschule for 1911-12. *Ledertechn. Rundschau,* 1912, 267-8. A classified abstract is given of 1,224 analyses, judgments and advices together with other activities of the Institute, which cannot well be condensed here. The range of inquiry and research was very broad, showing a great variety of problems, including many abnormal cases in practical work.

W. J. K.

Tanning among the Esquimaux. ROALD AMUNDSEN. *Ledertechn. Rundschau,* 1912, 268. Extracts from the German edition of Amundsen's "Northwest Passage" pertaining to this art are reprinted. For covering the kayaks or canoes, the skins of the female seal are prepared by the women; the flesh is scraped and the remainder of the fat removed by chewing. The fells are rolled up in bundles, hair out and kept over a low fire until the hair is loose and after removing this, the hides are preserved frozen until spring when they are stretched wet on the kayak frame, sewed and let dry. Many Esquimo tribes use urine in the treatment of hides. The further description of the processes used by the tribe here in question (the Netschjilli) show these to consist essentially in thorough cleaning and laborious mechanical working. W. J. K.

The Sugar Content of Tanning Materials and Extracts. JOH. PAESSLER. *Ledertechn. Rundschau,* 1912, 361-4, 369-72, 377-80. This subject was investigated in 1894 by v. Schroeder, Barthel and Schmitz-Dumont (*Dingl. polyt. Jour.,* Bd. 293, Heft 10) who used a modification of Allihn's Fehling reduction, after removing the tannins with basic lead acetate and the excess of lead with sod. sulphate. Cane sugar was determined only in quebracho extract, this being the only occurrence of importance at that time. Later Andreasch (*Gerber,* 1895-7) showed that substances of the cane sugar type were also important as fermentation acid formers in tanning liquors, and he determined total sugars after inversion. During the last year sugar determinations in the principal tanning agents have been carried out at the Freiberg Versuchsanstalt, following vonSchroeder's method. Strict adherence to details (JOURNAL, [7] 577) is imperative; the tannin must be completely removed before reduction, and precisely 30 minutes employed for boiling. The summary table (we omit the analytical tables) is computed for 100 parts tannin determined by both methods. The author's more scientific designation of "substances of the grape and cane sugar class" is here rendered throughout simply as grape and cane sugar.

	To 100 parts tannin							
	Non-tannins		Grape sugar		Cane sugar		Total sugar	
	filter	shake	filter	shake	filter	shake	filter	shake
Pine bark	69	93	29	33	12	14	41	47
Oak bark	60	74	27	30	0	0	27	30
Sumac	60	74	16	17	2	2	18	19
Myrobalans, seeded	35	49	17	18	0	0	17	18
Myrobalans	33	48	16	17	0	0	16	17
Dividivi	41	55	10	11	4	4	14	15
Mimosa bark	32	39	5.5	6	8	8.5	13.5	14.5
Valonea	37	49	11	12	0	0	11	12
Trillo	33	44	7	7.5	1.5	1.5	8.5	9
Mallet bark	19	29	3	3.5	2	2	5	5.5
Mangrove bark	25	30	1.5	2	1	1	2.5	3
Quebracho wood	8	14	1	1	1	1	2	2

Andreasch showed that lactic acid which occurs in liquors which have been longest used, results principally from the fermentation of the non-tans. The domestic tanning materials (pine, oak, sumac) are seen to be richest in non-tans. Grape sugar which produces acetic acid, is highest in pine and oak and cane sugar in pine (absent in oak) and mimosa.

Similar investigations were made upon extracts. From the table of analyses of 17 chestnut extracts computed on the basis of 60 per cent. water corresponding to the usual commercial strength of 25° B., the following types are selected:

	Tans		Non-tans		Grape sugar	Cane sugar	For tans = 100 non-tans		grape sugar		cane sugar	
	filt.	shake	filt.	shake	filt.	filt.	filt.	shake	filt.	shake	filt.	shake
Type I	34.1	32.2	5.1	7.0	1.2	0.9	15	22	3.5	3.7	2.6	2.6
Type II	30.0	28.5	10.0	11.5	3.6	2.0	33	40	12	13	7	7
Type III	26.5	25.6	12.7	13.6	5.6	2.3	48	53	21	22	9	9

Extracts of type I with low non-tans and sugars are rare (2 here); there were 10 of the usual type II and 4 of type III with high non-tans. Chestnut extracts have a very low ash, here 0.2 to 0.9 per cent.

Such variable ratios may be attributed to (1) variations in composition of wood used, (2) the extraction, (3) additions of molasses, etc. On comparing the analyses of 33 specimens of chestnut wood computed on 14.5 per cent. water (tabulated in full), great variations were found: tan content 8.1-17.2 (filter), 7.1-15.8 (shake); non-tans to 100 tannin, 10-47 (filter), 20-65 (shake) although preponderating at 15-20 (filter), 25-30 (shake). In many cases the low tannin corresponded to high non-tans and the samples appearing to be from young wood belonged to this class. Considerable difference in ratios is seen on comparing the analyses of a medium representative wood and extract respectively:

	Chestnut wood		Chestnut extract	
	filter	shake	filter	shake
Tans	10.0	9.2	30.0	28.5
Non-tans	1.7	2.5	9.5	11.0
Non-tans (tans = 100)	17	27.0	32.0	39.0

The amount of non-tans obtained from a given wood is not a constant, but depends upon the method of extraction used and is seen to be higher in the manufactured product as compared with an extract for chemical analysis. This same difference appears on comparing the richest woods and the strongest extracts but is not so marked with poor grades. Eitner (*Gerber*, 1895, p. 145) showed the influence of heat and pressure during extraction. The author has repeated these experiments with chestnut wood. The analyses of the extracts are all reckoned on the original wood (water = 14.5).

Atmospheres over-pressure	0	2	2	3	4	6
Hours extracted	—	1	2	1	1	1
Filter method: tans	12.2	12.3	11.7	11.8	10.5	9.5
non-tans	2.4	3.2	4.9	6.2	10.6	15.2
grape sugar	0.4	0.6	1.0	1.4	2.5	5.7
cane sugar	0.3	0.5	1.0	1.5	3.4	5.7
tans=100; non-tans	20	26	42	53	101	160
grape sugar	3.3	5.0	8.5	12	24	60
cane sugar	2.5	4.0	8.5	13	32	60
Shake method: tans	11.2	11.2	10.7	10.9	9.6	7.6
non-tans	3.4	4.3	5.9	7.1	11.5	17.1
tans=100; non-tans	30	38	55	65	120	225
grape sugar	3.6	5.4	9.3	13	26	75
cane sugar	2.7	4.5	9.3	14	35	75

Non-tans therefore increase on long extraction or increase of pressure and more rapidly than the tannin diminishes; also the sugars are increased. The amount of dissolved substance is greater on long extraction under pressure but the value of the extract is lowered.

The following analyses of two chestnut extracts indicate adulteration with sugars (molasses, etc.).

	I		II	
	Filter	Shake	Filter	Shake
Tans	21.2	19.6	25.6	23.8
Non-tans	18.5	20.1	21.8	23.6
Grape sugar	2.5		2.7	
Cane sugar	4.4		9.0	
Tans=100; non-tans	87	103	85	99
grape sugar	12	13	11	11
cane sugar	21	22	35	38

The tans are low, non-tans high, grape sugar normal, but cane sugar high. Since on pressure extraction both sugars increase, it may be concluded that here molasses has been added, lowering the efficient value.

Eleven samples of oak extract were similarly analyzed and results computed on 60 per cent. water. The ratio between tans and non-tans was much less variable than in the case of chestnut, because old wood is always used. The average results were: tans 25.5-27.5 (filter), 23.0-25.0 (shake); non-tans 13.5-11.5 (filter), 16-14 (shake); grape sugar 4.05, cane sugar 2.5-1.5 (shake). For 100 tans, non-tans = 42-53 (filter), 56-66 (shake). The few available analyses (filter) for oak wood showed 9.0-13.3 tans, 4.9-6.5 non-tans, 35-54 non-tans to 100 tans. A series of experiments upon the extraction of oak wood under pressure gave similar results (tabulated) to those with chestnut; the quality of the extract was lowered by prolonged heating at over 2 atmospheres over-pressure. The author has seldom found sugar additions in oak extracts.

Analyses of liquid and solid quebracho extracts are also tabulated. The normal liquid extracts may be represented by 34.5 tans, 3.5 non-tans, 60.0 water, 0.3 grape sugar, 0.2 cane sugar, 1.0 ash. An extract showing high non-tans 6.5, gave also high ash 3.0, suggesting mineral treatment. Another gave 28.7 tans, 10.7 non-tans, 12.2 grape sugar, 2.9 ash; if sugar had been added, the increase above normal would approximate that of the non-tans, but is actually much greater. The conclusion was that some other extract had been added and a qualitative test proved presence of myrobalans. Experiments upon pressure extraction of quebracho wood showed (confirming Eitner) that this was not so sensitive to high heat as chestnut and oak. At 4 atmospheres unfavorable non-tan ratios result and when such are found in pure extracts, as well as high sugars, excessive pressure extraction may be assumed; such extracts give inferior leather.

We condense below the 10th table of extract analyses (60 per cent. water):

Filter:	tans	24.3	28.1	27.5	27.9	24.4
	non-tans	13.4	11.0	12.0	11.3	15.2
	grape sugar	1.9	3.0	5.4	3.1	3.0
	cane sugar	1.5	1.2	0.0	2.5	0.9
	tans=100; non-tans	56	38	44	40	63
	grape sugar	7.5	10.8	19.6	11.1	12.6
	cane sugar	9.7	4.2	0.0	0.9	7.1
Shake:	tans	20.5	26.9	23.7	25.3	20.1
	non-tans	17.5	12.2	15.8	13.9	18.1
	tans=100; non-tans	84	45	67	54	91
	grape sugar	7.4	11.4	22.7	12.2	15.0
	cane sugar	7.4	4.4	0.0	1.0	4.0

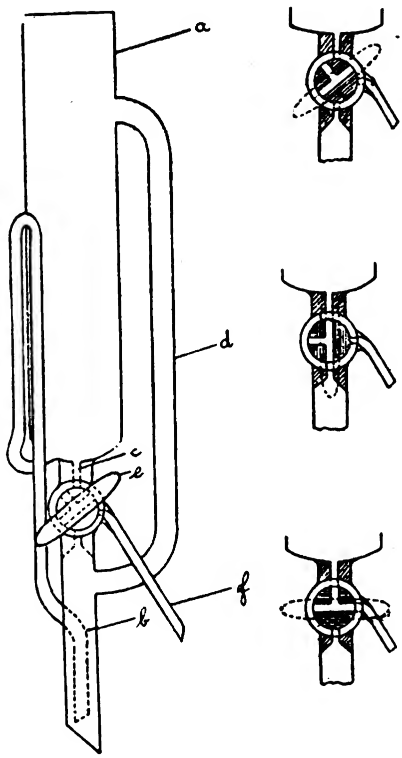
W. J. K.

Chrome Leather for Military Purposes. W. EITNER. *Gerber,* 1912 [38], 325-7. The recent decree of the French war ministry excluding two-bath chrome leathers is referred to and the *Leather Trades Review* article thereon (this JOURNAL [7], 627) quoted at length. In the opinion of the author, the sulphur which is objected to, is in the case of automobile pneumatic leathers essential to give the desired softness (fats being debarred) and to facilitate the vulcanizing process. The high sulphur content, which may reach 4.5 per cent. may be secured by a separate sulphur tannage. This is followed by a single bath tannage proper, securing the desired advantages of this process. The two-bath leather contains only 0.2-0.3 per cent. sulphur. The author tested sulphur leather which had been stored 6 years and found no deterioration whatever. The only tangible objection to sulphur is the tarnishing of metal and this might be prevented by lacquer. The evil effects of free sulphuric acid derived from the two-bath process are often much overrated. W. J. K.

Process for Vache Leather. *Gerber Courier,* Nov. 23, 1912. The writer recommends that the hides be hung in the limes, head down and changed daily into a stronger lime for 5 days, the temperature being kept as high as 52° F. The first liquors must not be as sour as for sole leather, or the product will not be sufficiently pliable and elastic. The hides should be hung in the liquors, head down, or if the vats are not deep enough, they may be hung over sticks, grain side out. There should be about 12 handlers in the series, gradually increasing in strength up to 13° barkometer, the hides remaining one day in each. A false floor should be floated on the liquor in the layaway vats, on which the first hides may be smoothly spread out, and the dusting material (½ pine and ½ oak bark), evenly distributed. The time for the first layer is 4 weeks, liquor 13° bk., temperature not below 75° F. Second layer, 20° bk., 4 weeks, dusting material pure oak, or oak and valonia. The hides are now washed, split into sides and dried. The drying must be carefully watched, and if the shanks become too dry they must be dampened. When the proper stage of drying is reached, both sides of the leather are brushed with a stiff brush and soft water, and then the grain is vigorously rubbed with a blunt wooden sleaker, until it is smooth and pliable. The sides are now spread on a table, flesh side up, and a dressing applied with a rough brush. The dressing is made by boiling 2 oz. China moss in 10 quarts water, and stirring in 2 lbs. flour, 2 lbs. kaolin and 4 oz. gambier. The grain is now thoroughly worked out with a somewhat sharp tool, wiped with a clean cloth, and lightly oiled with linseed oil. L. B.

Improved Soxhlet Extraction Apparatus. DR. H. SCHMID. *Chem. Ztg.*, No. 128, 1912, p. 1249. The Soxhlet shown in the diagrams has a 3-way cock *e*, by means of which the extract may be taken off at *f*, permitted

to run back through *c* to the boiling vessel, or siphoned back through *b*.



The apparatus has been patented in Germany and Switzerland and is obtainable from C. Desaga, Heidelberg.

Practical Notes for Leather Workers. *Leather Trades Review,* Dec. 8, 1912, p. 914. This article embraces sections on waterproofing, storage troubles, loss of gloss, economy in use of tan, dyes, color of chrome solutions, oils, spewing, and degras.

Manufacture of Chrome Sheep. *Leather Trades Review,* p. 918. Review of customary methods, including everything from raw skin to dyed and finished leather.

The Measurement of the Absorption of Oxygen by Sewage Effluents. H. J. S. Sand and S. R. Trotman. *J. S. C. I.*, XXXI, 1166, Dec. 31, 1912. The authors discuss the method of Letts and Adeney, in which the rate of absorption of oxygen is sought. They conclude that it is not prac-

ticable to measure the rate of absorption, and show that good duplicates can be obtained in measuring total absorption. A sample of the effluent was shaken for several hours in a bottle having a rubber stopper fitted with a cock. The decrease in volume of air in the bottle was then measured by connecting the bottle to a graduated tube. The authors regard this measurement as likely to prove valuable in the examination of sewage effluents. L. B.

Belting Leather. Vat Tannage with Extract. *Gerber-Courier*, Dec. 14. 1912. Extract liquors being deficient in acid, acid must be added but not mineral acids, as these endanger the toughness and firmness of the leather. Oak-wood and chestnut-wood extracts are suitable, the latter, however, having more color. To prepare a sour liquor with which to acidify the tan-liquor, some fir-bark is placed in a vat and covered with spent bark-liquor or water at 90° F. After 24 hours, 25 lbs. of bruised barley is added for each cwt. of bark, and the whole allowed to stand two weeks. A liquor of 6° Bé. is made from extract and enough of the sour liquor added to give a slight sour taste to the whole. After this addition the liquor should stand 6 days before use. The limed and cleaned hides are hung in a "coloring" liquor of 0.5° Bé. for one day. Five others follow: 0.6°, 1 day; 0.9°, 2 days; 1.2°, 3 days; 1.5°, 4 days; 1.8°, 6 days. These liquors must be sour enough to produce the necessary swelling. After 8 days preliminary treatment in a liquor of 1.8° Bé. containing fir bark, the hides are laid away for 40 days in vats with false bottoms (strength of liquor not stated). Once in two weeks the liquor is pumped out, tested, and made up to the original strength with extract. This may complete the tannage, or the leather may be filled to greater weight by laying away in a warm liquor (80° F.), of 2.5° Bé. for three months, the strength being restored every two weeks. When taken from the vats, the leather is washed in a wheel with warm water for ½ hour, scudded, brushed, oiled with fish oil and partly dried. It is then set out on tables with wooden sleakers to soften the grain, and dried ready for stuffing. This process is tiresome, slow and particular. If the leather is hard, tallow only is used; if it is somewhat soft, ⅓ stearin may be added. This is applied at about 190° F. to the warmed leather. In order to prevent the fat from striking through to the grain side and darkening the color, the leather may be laid grain down on a thick pad of burlap wet with cold water while the hot grease is applied to the flesh side. After stuffing, the leather is hung for 3 or 4 days in a bath of water or used sumac liquor to prevent the grease from spewing. After rinsing from this bath, a mixture of equal parts of tallow and fish oil is applied to the grain side before drying. L.B.

Process for Preparing Calf-skins for Tanning. *Shoe & Leather Reporter*. Dec. 26, 1912. The soaked and cleansed skins are coated with slaked lime and containing 6 per cent. red arsenic, of the consistency of thick paint, on the flesh side, folded once with the hair inside and piled in a

vat flesh to flesh and weighted down. The vat is filled with water and left five or six days, when the skins are unhaired. This process gives a smooth, fine grain. Fourteen pounds of lime and 5 lbs. red arsenic, slaked together, are used for liming 100 lbs. skins. This is done in a paddle, stirring 3 or 4 times a day for from 3 to 7 days. After washing from the lime, the skins are bated. Two pails of dry bran are put in water at 120° F. in the paddle and left over night. Next morning the bath is warmed to 95° F. and ½ pint lactic acid added for each 100 lbs. skins. Then the skins are thrown in and another ½ pint of acid added. After paddling for 3 or 4 hours the skins are taken out and washed in warm water. For a second lot of skins, the liquor is run down about a foot and filled up with water, heating to 95° and adding 1 pint lactic acid per 100 lbs. of skins but no fresh bran. After five repetitions the liquor is discarded and a fresh one made up. The bating may also be done with a solution of 8 lbs. salt and 2 lbs. salammoniac for each 100 lbs. skins. After bating the skins are pickled by drumming for 2 hours in 15 gallons of water and 5 lbs. salt for each 100 lbs. of skins. After starting the drum run in 15 lbs. of salt and from 2 to 4 lbs. sulphuric acid dissolved in 5 gal. water per 100 lbs. skins. If the skins are to be tanned with quebracho or other vegetable material formic acid should be used in the pickle, instead of sulphuric.

Notes on Dogskins. *Shoe & Leather Reporter,* Dec. 26, 1912. Wash the skin in water containing sal soda, then scrape it and work out the grease. Unhair by liming or by painting with sodium sulphide on the flesh side. After unhairing lime for a few days in clean fresh lime, to help in removing the grease. Dogskin makes a very durable glove leather when it has been thoroughly cleansed from grease, and tanned with chrome.

Some Notes on the Enzyms Concerned in the Puering or Bating Process. JOSEPH T. WOOD and DOUGLAS J. LAW. *J. S. C. I.,* XXXI, 1105-9, Dec. 16, 1912. The origin of the enzyms concerned in the process of puering with dog dung has been a matter of controversy. Eberle and Krall (abstr. this J., VI, 452) conclude that the tryptic ferment in the dung is unchanged trypsin secreted by the pancreas. Other investigators have concluded that the trypsin from the pancreas suffers putrefaction in the intestine and is not present in the large intestine. The authors examined the intestines of dogs so as to learn what enzyms were present at each stage of the digestive process. The dogs were killed by means of chloroform and carbon dioxide, and the entire digestive tract removed, and the various parts examined separately. The pancreatic juice as secreted does not contain trypsin, but is rendered active by the addition of another ferment secreted by the small intestine mainly at its upper end. The contents of the small intestine are active in alkaline solution but inactive in acid solution, while the contents of the large intestine are active in acid solution. The authors believe that this fact is due to the presence

of peptic enzyms secreted by bacteria in the large intestine. The peptic enzyms of the stomach are most active at an acidity corresponding to 0.2 per cent. HCl, while such a degree of acidity stops the action of the peptic enzyms of the large intestine. If the tryptic enzyms found in the large intestine are not due to bacterial action, they must be secreted by the walls of the intestine. The presence of a number of separate enzyms in the contents of the large intestine makes this improbable. Further evidence in favor of the belief that the enzyms of the puer are of bacterial origin is found in the fact that the puer as used is far more active than the contents of the large intestines of dogs. This can only be due to an increase of enzyms by fermentation going on in the puer. Quantitative determinations of the activity of the enzyms present in various parts of the digestive tract were made. L. B.

PATENTS.

Process for Making Lactic Acid. British Patent No. 17,275. O. FRIEDBERGER, Giessen, Germany.

Process for Making Mocha Leather. British Patent No. 18,573. M. JIROVSKY, Berlin, Germany. The method involves treatment with a mixture of lime and potash, then with dilute nitric acid, and finally with borax.

Process for Clarifying Tanning Extracts. British Patent No. 16,527. A. REDLICH, Vienna, Austria. Liquors, especially quebracho, are heated without access of air, preferably under pressure, and cooled with stirring. They throw down a flocculent deposit. The settled liquid may be concentrated to a cold-soluble extract.

Process for Rendering Leather Impermeable. British Patents Nos. 16,904 and 18,286 and French Patent No. 440,105. G. G. JOHNSTON, Sydney, Australia.

Treating Waste Leather. British Patent No. 15,561. E. BUE, Goussainville, France. Cements for hardening steel, charcoal for decolorizing purposes, and cyanides are made from waste leather.

Leather-staking Machine. U. S. Patent No. 1,043,050. A. C. LAYMAN, Wilmington, Del.

Nitrogen Dioxide in Ferric Tanning. U. S. Patent No. 1,048,294. JOSEPH BYSTRON, Teschen, Austria. The delimed hide, freed from acid, is placed in a solution of ferrous sulphate of 5 to 10° Bé. with or without common salt or other neutral salt of soda or potash. A current of dioxide of nitrogen is passed through, producing a basic ferric salt which is fixed on the hide fiber making a soft tough leather.

Treatment of Skins and Hides for the Removal of Fat, etc. F. LEHMANN, Germany. The skins are hung in an alkaline bath and electric current sent through.

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BOUND VOLUMES OF THE JOURNAL.

Vol. VII is now ready. Copies of all previous volumes are also on hand. See notice in last number.

LABORATORY EXTRACTION OF WOODS AND BARKS.

By Roy H. Wisdom.

The proposed Official Method for the extraction of woods, barks, and spent materials, as published in the June 1912 JOURNAL, reads as follows:—

Extraction:

Extraction shall be conducted in an apparatus consisting of a vessel in which water may be boiled and a container for the material to be extracted. This container shall be provided above with a condensation chamber so arranged that the water formed from the condensed steam will drip on the material to be extracted, and provided below with an arrangement of outlets such that the percolate may either be removed from the apparatus or be delivered to the boiling vessel. The boiling vessel must be so connected that it will deliver steam to the condensation chamber and that it may receive the percolate from the container. The condensation water from the condenser must be at approximately the boiling temperature when it comes in contact with the material to be extracted. The material of which the boiling flask is composed must be inert to the extractive solution. Suitable provision must be made for preventing any of the solid particles of the material from passing into the percolate.

Five hundred c. c. of the percolate shall be collected outside in approximately two hours and the extraction continued with 500

c. c. for 14 hours longer by the process of continuous extraction with reflux condenser. The applied heat shall be such as to give by condensation approximately 500 c. c. in 1½ hours.

There is one objection to the above method, viz., the 14 hours continuous extraction, thus making it necessary to run the extractor over-night. This disadvantage is apparent without further elucidation. Therefore if we can shorten the time of extraction to one working day and still obtain comparable results, we shall have improved the method to the extent that the entire operation may be performed under personal supervision.

A perusal of the results obtained by the 1907 Committee on Extraction of Tanning Materials and from which the present proposed method originated, shows that a comparison between the method recommended and one more along the lines suggested by the writer bears out the Chairman in his statement that "close scrutiny of the results would indicate that less than twelve hours total extraction would be inadvisable." Despite this fact, the writer was not fully convinced, and believed it possible to evolve a shorter method whereby the destruction of tannin by continued boiling would be reduced to a minimum, with a practically complete tannin extraction. With this idea in mind, he conducted a series of experiments covering a somewhat wider range than that touched upon by the Committee.

Let it be understood that the results shown below do not necessarily contradict nor dispute those obtained by the Committee. Let them rather be construed as a continuation of that work, inasmuch as the data then secured did not show a total extraction of this character with a duration of less than 12 hours. The Reed extractor was used, which conforms to the specifications with the possible exception of the statement that "the material of which the boiling flask is composed must be inert to the extractive solution," which matter will be dealt with later in this article. The five well-known tanning materials, chestnut wood, oak bark, hemlock bark, mangrove bark, and quebracho wood were used in the experiments and any method which will work satisfactorily on these should cover practically the entire field of woods and barks. The short method follows the proposed Official Method in every detail with the exception of 6 hours con-

tinuous extraction instead of 14 hours, thus making a total extraction of 8 hours as compared with 16 hours. The gelatine-salt test for tannin was completely ignored.

The results are herewith appended:—

Material		Total solids Hours		Soluble solids Hours		Insolubles Hours		Non-tannins Hours		Tannins Hours	
		8	16	8	16	8	16	8	16	8	16
Chestnut wood	1..	13.33	14.45	12.23	13.08	1.10	1.37	4.61	5.31	7.62	7.77
Chestnut wood	2..	12.22	13.83	11.37	12.53	0.85	1.30	3.94	4.89	7.43	7.64
Oak bark	1..	22.83	24.24	21.32	21.77	1.51	2.47	8.78	9.26	12.54	12.51
Oak bark	2..	20.76	20.95	18.92	19.00	1.84	1.95	8.93	9.44	9.99	9.56
Hemlock bark	1..	20.41	20.84	16.00	16.76	4.41	4.08	5.70	6.59	10.30	10.17
Hemlock bark	2..	20.18	19.67	16.65	16.28	3.53	3.39	5.06	5.18	11.59	11.10
Mangrove bark	1..	44.07	44.00	37.37	37.28	6.70	6.72	8.73	8.76	28.64	28.52
Mangrove bark	2..	52.52	52.46	51.28	51.16	1.24	1.30	7.25	7.40	44.03	43.76
Quebracho wood	1..	28.57	28.63	23.46	23.77	5.11	4.86	2.85	3.12	20.61	20.65
Quebracho wood	2..	29.30	29.21	24.93	24.92	4.37	4.29	2.87	2.93	22.06	21.99

As will be noted, two different samples of each material were tested and the analyses represent the mean of duplicate determinations.

The different tanning materials will be commented on in turn:—

Chestnut Wood:—

Without doubt the results here favor the longer extraction if tannin content alone is considered but the difference is so small as to be within the limit of personal error and completely overshadowed by the advantages of the short method.

Oak Bark:—

Here the advantage is slightly in favor of the short method, the lower non-tannins and insolubles overbalancing the difference in total extractive.

Hemlock Bark:—

Practically a duplicate of the Oak in comparable tannin results. Two peculiarities are apparent here; the longer method returning lower insolubles in both cases and in one case, lower total extractive.

Mangrove Bark:—

The short method here does not affect any single item to an appreciable extent.

Quebracho Wood:—

Comparable results very similar to those returned by the Hemlock Bark.

Summary:—

From these results it can readily be seen that the grounds for the proposed change are perfectly valid, and when one stops to consider that not less than 85 per cent. of the total amount of tannin is extracted in the first 500 c c., it is not unreasonable to look for a method which will extract the remaining 15 per cent. in 6 hours. The interesting table below, comparing the purity of the various extractions, shows very plainly the effect of continued boiling even of the weak solutions.

		Purity Hours	
Material		8	16
Chestnut wood	1	62.3	59.4
Chestnut wood	2	65.4	61.0
Oak bark	1	58.8	57.5
Oak bark	2	52.8	50.3
Hemlock bark	1	64.4	60.7
Hemlock bark	2	69.6	68.2
Mangrove bark	1	76.6	76.5
Mangrove bark	2	85.9	85.5
Quebracho wood	1	87.9	86.9
Quebracho wood	2	88.5	88.3

It is unfortunate that no Committee has been appointed this year to do any work in this line, for the unsupported work of one member can have but little weight unless verified by an authorized Committee.

Now in regard to the clause referred to earlier in this article that "the material of which the boiling flask is composed must be inert to the extractive solution," the assertion that not less than 85 per cent. (ascertained by actual analyses) of the total amount of tannin is extracted in the first 500 c. c., should dispose of this requirement which was aimed at the copper boiling receptacle. Copper has been shown to have a "decidedly detrimental effect upon tannin solutions upon continued boiling" but the results upon which this deduction was based were upon continuous extractions only and which did not remove the major portion of the tannin from further action. In fact, the Chairman stated at the time

that "It is possible that the same action takes place in a proportional degree in the weak solutions obtained in the continuous extraction process after removal of the stronger fractions, but if so, its effect upon the ultimate result is but slight."

However, in order to prove this, experiments were made using the Teas extractor connected with both glass and copper boiling receptacles. The results showed practically no difference and prove that the destruction of tannin shown in the above table is due entirely to continued boiling regardless as to whether the boiling flask is of copper or of glass.

Therefore unless this clause in the proposed Official Method is changed to read in effect that "the material of which the boiling flask is composed must be practically inert to the extractive solution remaining after the removal of the first 500 c. c. by outside condensation," it would seem to the writer that this would bar extractors of the Reed type and which would appear an unnecessary action.

NOTES ON DISCUSSION.*

By F. M. Loveland.

At the last annual meeting there were several questions brought up for discussion that were not cleared up at that time. While it is not the intention of the writer to express an opinion on these subjects, nevertheless, we have done some little work during the interval, that may be of passing interest to the Association. and it is offered in that spirit only.

One of the matters in question was in regard to the heavy white precipitate that settled out of a certain class of sulphite-cellulose extract. We have made an examination of this sediment and find the same to be sulphur. Mr. A. W. Hoppenstedt collaborated with us at that time, and I am sure will verify this statement.

There is another matter, which, while not coming under the same head, I desire to bring up at this time, and that is the detection of sulphite-Cellulose Extract in the finished leather.

* Read at the *A. L. C. A.* Convention, Washington, D. C., Dec. 6, 1912.

Dr. A. Gansser has already brought the question to attention in *Collegium*, No. 509, page 482. The Doctor tanned pieces of cow hide in extract liquors, so made up, that in one case 5 per cent. of all the extract used was Sulphite-Cellulose, and in another only 2 per cent. The finished leather was pulverized and water soluble made upon same. The solution when treated with aniline and HCl showed the characteristic flocculence of this test. However, his results are just the opposite of our own, and the Doctor used only 5 and 2 per cent. in admixture, while we worked with the straight extract in as high as 50° barkometer liquor. It would appear that different Sulphite-Cellulose extracts give results at variance by the same tests.

Messrs. Yocum and Faust found that by blending a certain sulphite-cellulose extract with other tanning extracts a large increase in insolubles occurred over the theoretical amount, with of course a loss of tannin, while Mr. Reed found the exact opposite. Mr. Faust also stated that he found entirely different results on two different brands.

Sometime since the writer was given a piece of leather, which was said to have been tanned with a blend of about half Quebracho and this extract, in combination. Desiring to verify this statement we made a water soluble on the leather, but could get no reaction by the Aniline- HCl. test. We came to the conclusion that either the extract changes during the process of leather manufacture, or that it was entirely soluble and had been previously washed out.

To fix the point, pieces of cow hide direct from the tannery beam house were started and tanned exclusively in this extract. The leather was bleached, oiled and finished in the regular way, except that the bleach was very mild, the leather simply being dipped and quickly removed. Water soluble was then made by the official method, and this tested against a weak solution of the extract with the following results. I might also add that we concentrated our water soluble solution one-half for the secondary tests and found them to bear out the first.

	Water soluble	Sulphite-cellulose extract
Gelatine-salt	Test	Test
Ferric chloride	Greenish coloration	Reddish brown coloration
Basic lead acetate	Precipitation	Precipitation
Aniline-HCl	Very clear	Test
Lime water	No change	No change
$SnCl_2$-HCl	*Cloudy	Clear

Extract solution clear at all times.

It is evident from the foregoing tabulation that the extract undergoes some change during the process of tanning. At least the water soluble does not respond to the same tests as the extract, and it would be impossible to detect it in leather by the Aniline-HCl method.

At the meeting a year ago considerable discussion took place after the reading of a paper by Mr. Alan A. Claflin on "The Tanning Properties of Waste Sulphite-Cellulose Liquors." The question led up to the discussion of non-tannins, and Mr. Oberfell, Mr. Reed and Mr. Small all mentioned the fact of difficulty in obtaining proper filtrates on several kinds of extract. The writer also mentioned the possibility that perhaps the ratio of non-tans to tannin might have some bearing on the subject, as in the case of fresh and spent Mangrove barks.

The writer had in mind that perhaps an excess of non-tans might have a masking effect on the absorbing power of the hide powder, and with a given amount of tannin the ratio of non-tans would play quite an important part in the result. Working along these lines we produced some results, that as I have said, seem interesting, but the work has not been carried far enough to make them conclusive.

Four kinds of extracts were used, viz., Chestnut, Mangrove, Hemlock and Myrobalan. The extracts were weighed out in separate bottles as for regular analyses, and almost an identical amount taken for each extract, so that the variations are not caused by the range between 0.35 per cent. and 0.45 per cent. tannin. They were also run under identical conditions, the same amount of hide being used and at the same time. A known amount of cane sugar, in solution, was added to each liter flask.

* The water soluble cleared up in excess HCl.

and the extracts dissolved at the proper temperature and dilution. In other words the extracts were treated as usual, except in the addition of non-tans in the form of sugar.

On the Chestnut extract the total solids were raised from 36.12 per cent. in the original to 42.47 per cent. on the last, with an increase of non-tans from 11.48 per cent. up to 19.95 per cent. The non-tans were not equal to the tannin and no loss occurred.

With the Mangrove the solids ranged from 46.46 per cent. to 56.93 per cent. and the non-tans 11.98 per cent. to 28.42 per cent. This brought the non-tans higher than the tannin and loss shows 0.43 per cent., 0.97 per cent., 1.20 per cent. as the non-tans grade upward. We find a loss on this extract with the non-tans lower than the tannin.

The Hemlock extract shows a minus tannin of 0.20 per cent. and 0.49 per cent., the non-tans building from 17.66 per cent. to 31.67 per cent. both non-tans in this case being higher than the tannin.

The Myrobalan extract had the non-tans raised in each case above the tannin and in the highest as far as 23.34 per cent. above it. This shows a loss in each case from 0.62 per cent., 0.76 per cent. up to 1.37 per cent.

In no case was the sugar absorbed by the hide and in each extract except the Chestnut a loss of tannin occurred. Perhaps the Chestnut would also show a loss if the non-tans were raised to a higher per cent. The following figures show the analyses of these extracts:

ANALYSES OF CHESTNUT EXTRACT.

	Extract	Extract and sugar				
Total solids	36.12	37.06	38.17	40.60	41.53	42.47
Soluble solids	35.95	36.90	38.01	40.36	41.38	42.23
Reds	0.17	0.16	0.16	0.24	0.15	0.24
Non-tans	11.48	12.91	14.49	17.18	18.56	19.95
Tannin	24.47	23.99	23.52	23.18	22.82	22.28
Corrected non-tans	—	11.37	11.48	11.31	11.33	11.45
Corrected tannin	—	24.58	24.47	24.64	24.62	24.50

ANALYSES OF MANGROVE AND HEMLOCK EXTRACTS.

	Mangrove extract				Hemlock extract		
	Extract	Extract and sugar			Extract	Extract and sugar	
Total solids	46.46	53.83	56.05	56.93	49.05	56.82	58.24
Soluble solids	46.28	53.72	55.86	56.81	47.50	55.63	57.03
Reds	0.18	0.11	0.19	0.12	1.55	1.19	1.21
Non-tans	11.98	23.76	26.94	28.42	17.66	29.46	31.67
Tannin	34.30	29.96	28.92	28.39	29.84	26.17	25.36
Corrected non-tans	—	12.41	12.95	13.18	—	17.86	18.15
Corrected tannin	—	33.87	33.33	33.10	—	29.64	29.35

ANALYSES OF MYROBALAN EXTRACT.

	Extract	Extract and sugar		
Total solids	88.54	90.71	90.99	91.67
Soluble solids	83.31	87.36	87.44	88.54
Reds	5.23	3.35	3.55	3.13
Non-tans	27.41	49.73	51.86	55.94
Tannin	55.90	37.63	35.58	32.60
Corrected non-tans	—	28.03	28.17	28.78
Corrected tannin	--	55.28	55.14	54.53

RESULTS OF THE SUGAR DETERMINATIONS ACCORDING TO THE DIRECTIONS OF THE COMMITTEE ON LEATHER ANALYSIS, A. L. C. A.[1]

By Dr. J. Paessler.

Results of sugar determinations on the aqueous extract of the oak leather, sample 1, and the hemlock leather, sample 2, sent to us are herewith submitted. They have been obtained with strict adherence in all essential points to the directions for experiment received by us. We deviated from the directions only in the two following evidently unimportant points.

1. The preparation of the aqueous leather extract was done as follows: Two portions of 30 gms. of leather each were placed after the removal of fat with petroleum ether in a Koch flask for 12 hours under pressure and then were extracted at 50° for 3 hours to 2 liters. This process employed at the Experiment Station corresponds very closely to that prescribed under B, Directions of the Committee on Leather Analysis, A. L. C. A. The

[1] Supplement to report published in December, 1912, JOURNAL.

process given under A for the preparation of the aqueous extract by extraction with the help of the Soxhlet apparatus at 50° could not be carried out because the apparatus required was not at our disposal. This process appears, moreover, extraordinarily troublesome and time consuming.

2. The solutions after removal of tannin with basic lead acetate and with normal lead acetate without and with addition of zinc oxide, having been freed from lead with an excess of potassium oxalate (10 g.) and inverted with hydrochloric acid, were rinsed into a 200 cc. flask for neutralization. After cooling they were neutralized after the addition of some phenolphthalein with sodium hydroxide and after cooling made to 200 cc. This procedure appeared more practical than that in the directions, according to which the solution should be neutralized with anhydrous sodium carbonate with the use of litmus paper. The percentage sugar content corresponding to the amounts of cuprous oxide obtained by the prescribed procedure could not be given in the summary because the tables of Munson and Walker were not at hand.

With the amounts of cuprous oxide which come into consideration in the experiments prescribed, the different tables for the calculation of the amounts of sugar, which depend upon the action of Fehling's solution upon sugar solutions, do not differ noticeably from one another. For the sake of comparison, in the case of the sugar determinations carried out as prescribed by the Committee on Leather Analysis, A. L. C. A., and those further to be mentioned, which were not carried out according to Prof. Von Schroeder (see later); the dextrose table belonging to the Meiss-Allihn sugar determination (60 cc. Fehling's solution, 145 cc. total liquid, after heating to boiling, duration of boiling 2 min.) according to E. Wein, was employed for the finding of the sugar content after the calculation of the cuprous oxide to copper.

In the following table are given the results in percentage of sugar, as they were obtained in the aqueous leather extracts treated with dextrose, after subtraction of those sugar amounts which the leather extract not treated with dextrose gave directly. The amount of sugar added according to directions (1.2 gms. per liter) corresponds to 8 per cent. of sugar calculated to leather.

TABLE.

8 per cent. dext added to the Leather extract	Leather extract precipitated with					
	Normal lead acetate		Basic lead acetate		Normal lead acetate + ZnO.	
I. Oak leather	8.42	8.32	6.65	6.50	8.65	8.30
	average 8.37		average 6.57		average 8.48	
II. Hemlock leather	8.65	8.74	6.85	6.67	8.59	8.45
	average 8.70		average 6.76		average 8.52	

From this table it appears that the results obtained by the use of normal lead acetate or of normal lead acetate and zinc oxide were found without exception higher than they must have been theoretically. On the other hand, results obtained with the use of basic lead acetate as precipitant, remain far below the theoretical calculated amount of sugar.

Since the results obtained in the present investigation with the basic lead acetate as precipitant did not agree with those obtained earlier by Prof. Von. Schroeder, according to whose procedure in the Experiment Station all the sugar determinations were carried out, the cause of the deviating results obtained according to the directions of the Committee on Leather Analysis was sought to some extent.

For this purpose, pure dextrose solution, obtained with the dextrose sent us, containing 1.2 gms. dext. per liter, both that obtained by the procedure previously described and also that obtained according to Prof. Von Schroeder, were treated with basic and normal lead acetate as precipitated in the same manner as if they contained tannin. The sugar contents were then calculated for comparison as if the sugar solution represented the aqueous extracts from the same amounts of leather as were used for the extracting of the leather sent in. The determinations were carried out both in the dextrose solution inverted as previously described and also in that which had not been inverted. Further, in the inverted pure dextrose solution which had not been treated with a precipitant, finally the sugar content in the pure dextrose solution and in the hemlock leather extract before and after the addition of dextrose (1.2 gms per liter) was found, according to Prof. Von Schroeder's procedure. According to this procedure the solution containing tannin is detanninized with basic lead

acetate and the filtrate freed from excess lead with Glauber's salt solution. The solution thus prepared is brought with 60 cc. Fehling's solution and water to the total volume of 145 cc. and heated one-half hour in the boiling water bath. The determination of the canesugar-like substances takes place in like manner after one-half hour's inversion of the prepared solution with sulphuric acid, 1 to 5, in the boiling water bath. The cuprous oxide obtained is oxidized to cupric oxide to destroy any organic matter which has been carried down and then reduced to metallic copper in a stream of hydrogen. The amount of sugar corresponding to the amounts of copper thus obtained are taken from the table of Koch and Ruhsam, also used in the official sugar determination procedure of the A. L. C. A.

The results obtained on the basis of these experiments are shown in the following table:

Dextrose Solution.

Solutions contain 8 per cent. dext. calc. to leather.

Hemlock leather extract.

	Normal lead acetate	Basic lead acetate	Without lead	Basic lead acetate
Procedure of	Inverted	Inverted	Inverted	
Com. Leather Ana.	8.27 8.36	5.04 5.14	8.26	
A. L. C. A.	avg. 8.31	avg. 5.09		—
	Not inverted	Not inverted		
	8.32	4.96		
Procedure accord.	Inverted	Inverted		*
Prof. Von Schroe-	8.00	8.21	—	Not inverted
der				7.95 7.95
				avg. 7.95

From the results of these experiments it is evident that according to the procedure of Prof. Von Schroeder; that is, with the use of basic lead acetate as precipitant and removal of the excess lead with Glauber's salt, quantities of sugar corresponding completely to the theoretical were found, both in pure dextrose solutions and also in the hemlock leather extract, while according to the procedure of the Committee on Leather Analysis, A. L. C. A., even in the pure dextrose solutions on the addition of basic lead acetate and removal of the lead with potassium oxalate much less

* Calculated from the difference of the amounts of cuprous oxide found in the hemlock leather extract before and after the addition of dextrose.

sugar was found than corresponds to theory. Since, now, on the one hand the dextrose solution without addition of the precipitant, but otherwise inverted according to the procedure of the Committee on Leather Analysis, A. L. C. A., gave the amount of sugar corresponding to theory (8.26 calc. per liter), and on the other hand the extract of oak leather previously prepared, precipitated with basic lead acetate according to the same procedure, but according to Prof. Von Schroeder heated one-half hour with Fehling's solution in a boiling water bath, gave a value far under theory (6.2 per cent. not given in the table), it is evident that the duration of heating of the prepared solution with Fehling's solution cannot be the cause of the too low results, but that this is to be sought in the simultaneous use of basic lead acetate and potassium oxalate as precipitant in that in this case considerable quantities of dextrose are carried down with the lead oxalate. The causes of this phenomenon, for which a theoretical explanation cannot be given off-hand, could not be followed further owing to lack of time.

Twenty-five cc. of the solution freed from tannin and from excess lead with potassium oxalate required in cc.

	Normal lead acetate	Basic lead acetate	Normal lead acetate + ZnO.
I.—Oak leather.			
Without dextrose	3.8 N/10 solution	0.05 N/10 solution	0.05 N/10 acid
With dextrose	—	—	—
II.—Hemlock leather.			
Without dextrose	3.0 N/10 solution	0.2 N/10 acid	0.1 N/10 soln.
With dextrose	2.9 N/10 solution	0.2 N/10 acid	0.1 N/10 soln.

The solution reacted afterwards in several cases weakly alkaline towards phenolthalein.

DISINFECTION OF HIDES AND SKINS.

Discussion at the Washington Convention, A. L. C. A., Dec. 7, 1912.

Mr. H. C. Reed, Secretary, read a letter from Mr. Alfred Seymour-Jones, extracts from which follow:—

"The questions surrounding the proper conservation of hides and skins are becoming more and more pressing, and I hope will be fully discussed at the Congress. I enclose a copy of the

report of the International Commission."[1] (Mr. Jones then summarizes the work of Abt and Becker on salt stains. See JOURNAL, for Sept. 1912.) "The conservation of hides and skins, especially those from overseas, which bring into our different countries diseases which are not indigenous, and which each spends millions of dollars annually to exterminate, and yet continually keep on importing, requires very careful consideration, and our efforts should be directed to co-öperation with the various government authorities, instead of allowing them to act, on false evidence too often.

"The Formic-mercury process seems to offer the best opportunity to the tanner for the conservation and sterilization of his hides and skins, either when imported from abroad or at home. The investigation, apart from my own work, has been completed by Dr. Ponder on behalf of the Leather Sellers Company, London. I enclose for the benefit of the Congress a copy of Dr. Ponder's report and his article to the Lancet. The method has been also confirmed by several continental scientists.

"The effect on the hide or skin has been favorably reported on by Prof. Procter, Dr. Stiasny, and Dr. Parker, who through his assistant Mr. Blockey, published a full report on results obtained at the Leather Sellers Technical College on various dried hides, on which he showed a very substantial gain in weight by using the Formic softening process. The results are published in full in the Tanner's Year Book for 1912.[2] I am informed that, many Tanners in England and on the Continent are at present using the process with great advantage. The cost of the process as being under one penny per hide was verified by the Experts sent down to Sir William Howell Davies' tannery in Bristol, by the Committee appointed by Parliament on Foot and Mouth Disease."

"The question of restraint of trade by adopting such a process has been cleared out of the way, and there remains no valid reason why the method should not be adopted internationally. I do not claim that it is the only method, but it is at present the only method which complies with all the conditions demanded by Gov-

[1] Condensed report appeared in this JOURNAL, Sept., 1912, p. 487-92.

[2] JOURNAL, Sept., 1912, p. 467-74.

ernment and those engaged in the various trades interested, be it hides, skins, wool, hair, rags, etc. The cost of the restoration of the dried hides to the wet salted condition will (if the scheme as suggested is adopted) fall on the exporter, as salting does at present."

Mr. J. H. Yocum, commenting on the formic-mercury process, expressed the opinion that the difficulty of removing the free formic acid from the skins would prevent the working of the sweating process. Formic acid is a powerful antiseptic and a small amount would suffice to prevent the growth of the bacteria on which the unhairing depends. The process in which bichloride of mercury is used in saturated salt solution is equally efficient for disinfection, and these salts are worked out in the milling process so as not to hinder the sweating process.

Mr. V. A. Wallin asked whether Mr. Yocum was sure that formic acid treatment would affect the sweating process.

Mr. Yocum replied that some tanners who had tried the process objected to the "rubbery" feel of the hides after it, which has been ascribed to the acid remaining in the hides, but that he could not be sure that this acid would hinder the sweating process.

Mr. Wallin asked further, whether if it were shown that the formic process does not hinder sweating, it would be a desirable method of sterilization.

Mr. Yocum said it would, and expressed his belief that the method is the best yet devised. In answer to a question from Mr. Griffith he said that the objection to the process on the part of European tanners is due to the unsatisfactory feel of the hides when they go into the limes.

Mr. Wallin said that some cases of anthrax had developed in Grand Rapids, within three or four years past, and the patients would probably have died but for the treatment given by a man who had studied the disease in China. The matter is a very serious one, and tanners would be very glad if imported hides could be thoroughly sterilized.

Mr. R. W. Griffith suggested that any antiseptic might interfere with sweating.

Mr. Yocum replied that saline substances can be removed by

soaking and milling while free acid forms a combination with the hide which is not broken down in these processes.

Mr. William Klaber suggested than an oxidizing alkaline substance, such as sodium perborate might be effective to neutralize the formic acid left in the skins.

Mr. W. H. Teas believed it not practicable to neutralize the formic acid left in the hide so as to obviate its sterilizing effect.

Mr. Yocum explained that Mr. Seymour-Jones recommends that the formic-mercury process be applied to the hides at the port of shipment, and that they be then shipped as wet-salted hides. While the same process may be used in the soaks at the tannery this would not prevent the possibility of infection from the hides in transit. The men who handle the hides may contract the disease by eating their lunch in the hide cellar, or by scratching their faces or arms with infected hands.

USE OF CHROMED GELATIN IN TANNIN ANALYSIS.

Method of Dr. E. Giusiana.

This new method of tannin analysis is briefly described in *La Halle aux Cuirs,* 1913, technical part, p. 17. (It may be noted that two other new methods of tannin analysis are given among the abstracts in this number of the JOURNAL.) Dr. Giusiana proposes to replace hide powder with fish glue or gelatin, previously tanned in a basic chrome solution prepared from 100 grams chrome alum crystals, 1 liter of water and 15 g. sal soda. Thin leaves of pure gelatin, white and transparent, are placed in this solution for 24 hours, when they will be found completely tanned and quite insoluble in hot water. They are then washed and neutralized in a 1 per cent. ammonia solution, again thoroughly washed, and dried between filter papers. The tanned gelatin may be kept indefinitely in a flask of distilled water. For 100 cc of tannin solution, the equivalent of 5 grams of dry gelatin is used. The shaking, filtration, etc., are as in the hide powder method.

ABSTRACTS.

The Rational Use of Spent Tan as Fuel. THEODOR BUDISCHOWSKI. *Allgemeine Gerber-Zeitung*, Jan. 25, 1913. Too little attention has been paid to utilizing spent materials in such a manner as to get the most fuel value. Many tanneries do not burn the tan at all, but haul countless wagon-loads of coal to their boilers past huge piles of old bark. A cubic yard of freshly leached bark weighs 1,100-1,200 pounds and contains from 75 to 85 per cent. water, or a little less in the case of wood. A good tan-press will reduce this to about 60 per cent. To feel the pressed bark, one would scarcely credit this, but it is easy to estimate by weighing a small quantity, drying and reweighing. Good air-dry bark has more than 10 per cent. of moisture. Rotten or frozen tan is worse than useless as fuel, and the many wet materials from cleaning vats, etc., which must for the most part be burned to get rid of them do not help to save coal. Thus it frequently happens that the combustion is very imperfect, and the spent tan seems to be comparatively useless as fuel. Of recent times, many processes have been devised for producing complete combustion, but none of them meet the principal difficulty, the fact that wet tan must be burned. When the material with its 60 per cent. or more of water is brought on to a moving or stationary grate, this great mass of water must first be evaporated, and then the steam raised to the burning temperature and drawn off with the gases of combustion. To do this a great quantity of heat is necessary, which must be subtracted from the heat of combustion of the bark. The heat value of dry spent tan is about —— B. t. u. per pound. When the bark has 60 per cent. water, the heat value is scarcely one-third as great. It is evident, therefore, that the first problem to be solved in order to make profitable use of spent tan for fuel, is how to dry it economically. The author has obtained good results with a slowly revolving drum placed over the boiler, through which the spent tan passes. An exhaust fan draws the gases of combustion through this drum, and the dried material is delivered directly into the stoking apparatus. The cost of repairs and maintenance of the apparatus is very slight, and the power required to operate it small. One hundred pounds of the dried tan are equivalent to from 25 to 30 pounds of coal. In operation, the apparatus is continuous and automatic, and the smoke-gases are expelled at a comparatively low temperature, thus utilizing their heat to the greatest advantage. L. B.

Frozen Extract. W. EITNER. *Gerber*, Feb. 1, 1913, Vol. 39, p. 29. It is often stated that extract which has been frozen does not give as good results, particularly in the matter of color, as the original extract. Recently a similar complaint came to the writer, in which it was asserted that when extract was used which had lain a long while in the open air, the rendement was lower than usual. In extract casks of the ordinary form and size, only a part of the extract contained ever freezes. In such a case after melting the frozen part, the extract was tested with a hydrometer and found to have fallen from 24.2° Bé. to 18.5°. The tannin

content fell from 23.24 to 19.82 per cent., less in proportion than the density. The original extract showed 0.65 per cent. insoluble, while the thawed out sample contained only traces. On examining a cask which had been frozen and melted again, it was found that the top part was less dense than the bottom, and on taking samples at various depths it was found that the insolubles increased from top to bottom, being 1.78 per cent. at the bottom. The writer attributes this to the gradual settling out of the less soluble materials with the gradual fall of temperature which preceded freezing. This process also brings about a decolorization of the extract. The less soluble portions of the tannin in an extract are in general darker in color than the more soluble portions, which fact serves to explain the clarifying effect of cold. Eitner explains the low rendement produced by extract which has been frozen by supposing that the difficultly soluble portions of the extract thrown out by cold become massed together, and do not return into solution when the temperature rises, and that these parts are those which give the extract its chief weight-giving properties, while the more easily soluble parts which remain in solution are those which penetrate and tan without filling up so well. The change of the difficultly soluble parts of a tanning material into freely soluble material by the sulphiting process changes its character radically, so that its filling and weight-giving properties are diminished. When extract which has been frozen and thawed is put directly into liquors, the difficult-soluble portion not only fails to dissolve and aid in the tanning, it even hinders, by filling up the pores of the hide, and also by accumulating on the surface and causing dark spots or otherwise spoiling the color. The difficulties caused by cloudy liquors are helped by keeping the liquor in motion. Eitner attributes the low rendement from extract which has been stored in open tanks to the low temperatures to which it is thus exposed, and suggests that in such a case it should be heated thoroughly before being diluted. If the whole is brought to the boiling temperature and held there for 15 minutes, the original relation between the more and less soluble parts of the tannin is restored. L. B.

Salt Stains. R. WEBER. *Technikum, Ledermarkt*, 1912, Nos. 27 and 34. The salt stains which the author has examined he attributes to the sulphate of lime in the salt, and not to bacteria. Bacteria do cause damage to hides, but of a different sort. The sulphate of lime is actually absorbed by the hide, more especially on the grain side. The rusty color of the stains is due to iron contained in the sulphate of lime. Skins salted with chemically pure salt were not stained in 8 weeks, but where particles of pure sulphate of lime had been placed, stains appeared, even though the salt had been sterilized, and they appeared also in the absence of iron. The author proposes that salt used on hides shall be freed from all traces of sulphate. A hide was treated for 3 days with 1 per cent. HCl to remove all phosphates, then washed and sterilized for 3 days with 1 per cent. corrosive sublimate, then immediately saltetd with sterile salt.

Particles of sulphate of lime were placed on the flesh side, and at these places stains formed, the formation of phosphates by bacteria being prevented by 0.1 per cent. sublimate in the salt. L. B.

Tanning Methods in Northern Nigeria. VICE CONSUL R. P. DOUGHERTY, Freetown, Sierra Leone. *Consular Reports.* According to a report published in the Government Gazette of Northern Nigeria, the hide and skin trade of that country is extensive. It is estimated that the exports of dressed goat and sheep skins amount to 1,000,000 per annum, the majority of which are goatskins. The sheepskins exported form 10 per cent. of the total.

The natives use simple processes of flaying and tanning. The ordinary flaying knives are made of soft iron and must be sharpened many times in skinning a single animal. An effort is being made to introduce an English steel flaying knife of moderate cost. Better flaying will remedy most of the defects in hides prepared by natives. Tanning is accomplished by placing the hides in water mixed with the ashes of certain trees, such as the tamarind. After two days the skins are stretched and then scraped with a blunt knife to remove the hair; they are sometimes washed in a solution made from the pounded pods of the *Acacia arabica.* It is stated that the pods contain a lining of pure tannin. Most of the skins are colored red by means of a dye obtained by mixing the pounded stalk of a form of millet with potash water. The skins are immersed for a few minutes and then hung up to dry. The dye may be fixed by soaking the skins a second time in the original tanning solution.

A large amount of the leather produced is used by the natives themselves in making ornamental saddlery, boots, sandals, bags, cushions, etc. Many of these articles are for actual use and others are designed for curios.

Practical Notes on the Tanning and Finishing of Sheep Leather. *S. & L. Rep.*, Jan. 23, 1913. Complete removal of sodium sulphide before pickling is essential. Drenching with bran drench or lactic acid or a combination of these is better than puering. After pickling with acid and salt, the grease should be removed by wringing or by solvents, and the skins drummed in warm salt water. Next pickle with salt and sulphate of alumina. After chrome tanning the skins, preferably by the one-bath process, they are drained, shaved and drummed in a weak bath of lactic acid and water, then dried. Then the skins may be wet up and finished at any time afterward. Coloring should precede fat-liquoring except in the case of black. When the leather is loose and spongy it does not color easily, the color soaking through instead of remaining mostly on the surface. This spongy character is apt to be caused by too much salt in the tan liquor. The best sheepskin leather is made from green salted pelts. Dry pelts should be thoroughly soaked before dewooling. It is generally advisable to finish dry skins on the flesh side, for gloves and linings, but if the grain is sound they make good grain leather also. Loose grain is a frequent fault of sheep leather and is often caused by too strong depilatory.

A Standard Viscosimeter. W. F. FARAGHER, *J. Ind. and Eng. Chem.*, Feb., 1913, p. 167. The writer comments on the defects of several forms of viscosimeters; commends the suggestion of Dunstan and Strevens (Jan. JOURNAL, p. 49), that the viscosity of lubricating oils be tested at various temperatures, and suggests that a standard instrument be adopted. He seems to favor the Engler.

The Consulting Chemist and the Leather Industry. ALAN A. CLAFLIN, *S. & L. Rep.*, Jan. 16, p. 27. It is comparatively easy to be an analyst to the leather trade, but it requires years of experience to be of use as a consulting chemist to the trade. It requires much more judgment and experience to interpret analysis than to make it. The manufacturer should not expect to get a recipe for making the best leather in the world from his consulting chemist, nor how to cut the cost of his chemicals in half, nor how to match a sample of his competitor's leather. Nor should he expect to be helped by his consulting chemist unless he places the entire case before his scientific counsel as completely as he would before his legal counsel. The consulting chemist should be able to give him exact facts as to cost of processes and amount of leather to be expected from given raw materials. He should also be able to point out the best way to secure highest efficiency in all departments except, perhaps, the selling department.

The Analysis of Vegetable Tanned Leather. B. KOHNSTEIN, *Allgemeine Gerber-Zeitung*, Nov. 9. 1912, Vol. XIV, No. 45, p. 5. *Total water-soluble*: Thirty grams of leather stand 12 hours in a percolator with water at 40° C. One liter of solution is then collected. If the leather is greasy, it should be first degreased. An aliquot part of the solution is evaporated, for total water soluble, and the residue ashed for soluble inorganic matter. Another portion is used to determine tannin and non-tans, and still another to estimate sugar content and the kind of tanning material used in making the leather. *Sugar*: Three hundred cc. of the solution is shaken in an Erlenmeyer with 4 g. freshly ignited pure MgO, and then heated with a reflux condenser, then stands 3 or 4 hours corked, is then well shaken and filtered. The filtrate must be free from tannin. One hundred cc. are evaporated, dried and weighed. The residue is then ashed, to determine how much of the previously determined inorganic matter is not taken up by magnesia. The difference between the total water-soluble and the residue from the magnesia filtrate enables us to estimate how much of the former is tannin and coloring matter. A high residue from the magnesia filtrate indicates loaded leather. Experience based on a large number of analyses indicates for pine and oak tannages the following figures (percentages):

	Pine	Oak	
	Vat tannage	Vat tannage	Drum tannage (Vache leather)
Water Soluble	8.0	3.5-4.0	14.0-15.0
Matter not taken up by magnesia...	3.0-4.0	3.5-4.0	5.0
Matter reducing Fehling's Solution, estimated as grape-sugar	1.2	0.7	1.0-1.02

It is thus apparent that the quantity of organic material which does not combine with magnesia does not point to a dependable conclusion in regard to the presence of added glucose. As a preliminary test for grape-sugar in the filtrate from magnesia, to 20 cc. of the filtrate add 1 cc. of 10 per cent. NaOH and one drop of freshly prepared solution of orthonitrophenylpropiolic acid. The indigo which forms colors the solution deep blue, and after a time the indigotin settles as a precipitate. The solution is now shaken with 20 cc. of chloroform, in which the indigo dissolves with a violet color. The intensity of this color, by comparison with standards, may be used for quantitative determination. The gravimetric determination of the grape-sugar is made with 50 cc. of the filtrate from the magnesia, added in a porcelain dish to 40 cc. Fehling's solution made up as follows: (a) 34.6 g. copper sulphate in 500 cc. water, (b) 173 g. tartrate of sodium and potassium and 125 g. solid potassium hydroxide to 500 cc. water. The Fehling's solution is raised to boiling, the 50 cc. of the solution to be tested slowly added, and the whole boiled 5 minutes. The cuprous oxide is filtered off, reduced to metal in a current of hydrogen, weighed, and calculated to grape-sugar by Allihn's table. In case the leather contains materials liable to be precipitated with the cuprous oxide, it is advisable to dissolve the precipitate in dilute HCl, precipitate the copper with H_2S, heat with sulphur in a current of H or CO_2 in a Rose crucible, and weigh as sulphide. The process for detannization with basic lead acetate is as follows: to 200 cc. of the original extract (from 30 g. leather as above) add 20 cc. lead acetate solution, prepared by digesting 100 g. lead acetate and 100 g. litharge with 500 cc. water and filtering. To 150 cc. of the filtrate from the lead acetate precipitate, 20 cc. of a 10 per cent. solution of sodium sulphate are added. When the precipitate has settled the solution is filtered. A portion of the filtrate is treated at once with Fehling's solution, and another portion (50 cc.), inverted by boiling for 2 hours under a reflux condenser with 5 cc. HCl, then nearly neutralized with NaOH, and treated with Fehling's solution in the same manner as the other portion. *Fats*: In a Soxhlet, 15 g. of finely pulverized leather are extracted for 6 hours with petroleum ether, 50° boiling point; evaporate the ether to constant weight. *Nitrogen*: Wilmarth's modification of Kjeldahl's method. One gram of pulverized leather is put into a 500 cc. flask with 20 cc. conc. H_2SO_4 and about 1 g. of mercury and digested until colorless. After cooling, 250 cc. water is added, and enough K_2S solution (5 per cent.) to precipitate the mercury, and 80 cc. of NaOH solution, sp. gr. 1.35, and a little granulated zinc. The whole is now distilled into ½ normal sulphuric acid, and the excess titrated with 1/10 normal baryta solution, methyl-orange indicator. *Determination of the kind of tanning material in the leather*: To test for the presence of pyrogallol tannin, a portion of the leather extract is boiled under a reflux condenser with formaldehyde and hydrochloric acid, well cooled and filtered. Sodium acetate and iron alum added to the filtrate show myrobalans or other pyrogallol tannins. Quebracho or mimosa tannage may be shown by placing a

drop of sulphuric acid on a rod moistened with the extract, causing a purple color, passing into violet. Other materials, especially pine and quebracho in mixtures with mangrove, may be recognized by the alcutin test. (See *Collegium*, 1912, p. 153, and this J., Vol. 7, 449 and 565.)

L. B.

Spew on Leather. B. KOHNSTEIN, *Allgemeine Gerber-Zeitung*, 1912, No. 49, pp. 2-3; No. 50, pp. 1-2; No. 51, pp. 2-3. Deposits on leather may be of mineral matter, as sulphur or crystals of hygroscopic salts, or crystals of fatty bodies, as stearic acid or free fatty acids with high melting point, rosin or paraffin, or finally molds which destroy the grain. With change of temperature or moisture content of the air, a deposit may form on the leather as it lies in the warehouse, or even after it has been made into shoes and been placed in the showcase of the shoe dealer. This is especially true of chrome tannages, on which deposits of mineral crystals or of fat are liable to form. It is the business of the leather chemist to discover the causes of these faults and devise means to avoid them. Much of the blame for spewing has been laid on the soaps and fats employed. Among those used for chrome leather are neutral soaps or animal residues containing oleic acid as liquid oils, such as neats-foot, and liquid animal waxes, such as spermaceti, and finally the so-called sulphonated products. In order to furnish these products free from stearides, the oils are expressed at low temperatures, and called winter-pressed. (Here follow details of the properties of sperm and neatsfoot oils.) Moulds often cause spots and stains on all kinds of leather, and they also cause fat-spewing because of their splitting action on fats. Chrome leather which has been fat-liquored and been laid away in mouldy bran or sawdust or has lain too long in pile may have such spots, the fat having been forced to the surface by the heating of the leather. Several kinds of moulds which cause trouble are named. When the microscope shows the absence of moulds, and no other cause can be found for spewing, it is often blamed on the natural fat of the skins. This may be the cause in the case of some chrome leathers which have not been thoroughly limed, and the spewing is most likely to cause trouble in the case of goods which are to be enameled, in which case the leather should be degreased by the use of a solvent; benzine, carbon tetrachloride, or a mixture of the two. The appearance of fat-spew on chrome goat and kid at low temperatures was so general that it was taken as a matter of course, something that belonged to any proper chrome tannage, like the bloom on oak sole or the trace of grease on genuine red Russia. The careful work of investigators has thrown much light on the causes of spewing, so that much less leather is now found in the market with this defect than formerly. Sometimes on goat or kip roundish spots on the neck or belly are free from the fat-spew which covers the rest of the goods. This is caused by imperfect fleshing, the spots on which the flesh was left being thicker do not tan perfectly, and so are harder than the rest and in the stuffing process do not get a full share of fat. Round

spots of fat occur on chrome leather, in size from 1/50 to ¼ inch, strewed about, often in chains or formless groups. The microscope shows no mould forms, but a crystalline or amorphous structure. The material burns without residue, with a smoky flame and characteristic odor. Such spots are due to the use of wool-grease (which is really an animal wax) in the fat-liquor. In general the presence of fatty acids having a high melting point tends to the formation of fat-spew. The tanner washes his leather carefully to remove traces of acid and acid salts. If any acid is left in the leather, as the stock dries, this remaining acid is concentrated, and damages the leather, making it tender and the grain brittle. The acid also causes fat-spew, by splitting up the soap or oil emulsions, releasing fatty acids, which because of their high melting point appear on the surface as fat-masses or white crystalline deposits with a fatty feel. The old tanners avoided iron sulphate for blacking leather because the freed sulphuric acid causes brittle leather and also spew of fatty acids. The makers of belt leather and automobile leather wash their wares with special care because the presence of free acid in a leather which must be exposed to heat is sure to cause rotting of the fiber. In the case of chrome leather used in shoes, free acid rots the stitching also. Several microörganisms are mentioned which are known to be able to split fats. The crystalline deposits formed on the surface of chrome leather which has been fat-liquored with oils containing wool-grease consist largely of cholesterin. Bone oil, which closely resembles neatsfoot oil and is often mixed with it, contains small amounts of cholesterin, and may therefore cause the same kind of spew as wool-grease. Means of determining wool-grease, by treatment with acetic anhydride to form acetic-cholesterol-ether, are described. When wool-grease is present, spewing may be prevented by additional oils (hydrocarbons) which hold the high melting point fatty acids in solution.

L. B.

A Suggestion for the Rapid Estimation of Tannin and Acidity in Tanning Liquors. RUDOLF VANICEK, *Zeitschr. f. angew. Chem.*, 26, auf. Teil, pp. 68-70. The author states that the total tannin from any given material as determined by the hide powder method consists partly of tannic acid and partly of substances which are neutral, *i. e.*, neither acid nor alkaline. He gives figures for seven samples, showing the proportion of total tannin which is tannic acid (figures are percentages): pine bark *a*, 49.9; pine bark *b*, 50.1; oak bark *a*, 61.3; oak bark *b*, 63.4; oak bark *c*, 99.8; sumac, 85.7; quebracho, 88.2. Dr. Vanicek assumes that in the case of any given material the ratio of tannic acid to total tannin is constant. He proposes to titrate the original liquor with N/10 soda and phenolphthalein, "spotting out" on paper; then to detannize a portion of the liquor with gelatin and again titrate, and then to calculate the difference to tannic acid, and by means of a previously determined factor for the particular tannin under examination to convert this tannic acid figure to total tannin. L. B.

Use of Lactic Acid for Chrome Tanned Leather. *Anon.* *Conceria*, 20, 272. In employing lactic acid for maceration of calf skins, about 1 part of the acid should be used to 100 parts of H_2O; somewhat less acid may be used in case of weak liming. The skins are treated in a vat at a temperature of about 30-35° C.; the temperature should therefore be about 40° C. before introduction of the skins. Slightly less lactic acid should be used for ram skins than for calf skins; a greater degree of swelling may be secured by reducing the temperature somewhat. Better results are obtained in all cases if the skins are washed after maceration and before introducing into the chrome liquor.

H. S. PAINE.

Rapid Method for Approximate Analysis of Tan Liquor. *Anon.* *Conceria*, 20, 129. Glass cylinders with graduations at 12.5, 25.0, 37.5, and 50 cc. are provided. The tan liquor (cold) to be tested is added to the 12.5 cc. mark, then dist. H_2O to 25 cc., and finally clear lime H_2O (saturated solution) to the 50 cc. mark. Shake, and examine every 5 minutes. If no precipitation occurs in 15 minutes, the solution is rejected and the test repeated with diluted liquor. Dilution is repeated until a separation occurs within 15 minutes; the strength of the liquor may then be calculated from the volume of the precipitate or supernatant clear liquid and the dilution of the original liquor. Variation in temperature due to the season of the year affects the result, as does also the degree of dilution; the method loses rapidly in accuracy, when the dilution is more than 6 fold. The dilution, if any, should be such that the liquor as tested does not contain more than 0.15 per cent. tanning material. The tan liquor does not need to be clear and does not require filtering, although it should be free from dense suspensions.

H. S. PAINE.

Experience with Sodium Monosulfide and Lime Vats Arranged in Series. *Anon.* *Conceria*, 20, 412. The lime vats were arranged in series of 6 and the hides were allowed to remain 1 day in each, liming thus requiring 6 days for completion. The proportion of 140 l. of lime to 100 salted green hides and 80 g of Na monosulfide per hide gave the best results. Strong liming was necessary in order to eliminate the fat, while the monosulfide caused the hides to swell and facilitated removal of the lime, the latter being readily washed out after the treatment. Before immersing the hides each day, the contents of the vat should be stirred in order to prevent the sediment from remaining attached to the bottom. The 6th vat contained H_2O at 22°; after removal therefrom the hides were depilated. After this treatment the hides were readily tanned; the leather produced was strong with a smooth, brilliant finish.

H. S. PAINE.

PATENTS.

Enameled Leather Softener and Process of Making the Same. U. S. Patent No. 1,049,674. L. L. COLMEAU, Haverhill, Mass. The mixture contains neats-foot oil, dissolved soap, alcohol and kerosene.

Process of Manufacturing Artificial Leather. U. S. Patent No. 1,048,342. E. REIDEL, Mannheim, Germany. The materials are animal refuse of various sorts, tendons, intestines, etc.

Manufacturing Alcohol from Sulphite Liquors. U. S. Patent No. 1,050,723. P. G. ECKSTROM, Sweden.

Staking Machine. British Patent No. 22,444. MOENUS COMPANY, Frankfurt a M., Germany.

Method of Cleansing Hides. British Patent No. 18,770. OTTO RÖHM, Darmstadt, Germany. After preliminary treatment with an alkaline solution, solutions of tryptases are employed.

Chrome Tannage of Sole Leather. French Patent No. 440,736. M. P. CASTIAN. A combination tannage is effected by using both chrome and vegetable tannin in the same bath. The leather is stuffed with paraffin and rosin, which is washed out of the grain by brief immersion in benzine, and brushing.

Leather Measuring Machine. British Patent No. 22,597. G. A. SCHETTLER, Leicester. The machine prints area and thickness on each piece measured.

Leather-working Machine. British Patents Nos. 22,806 and 22,807. D. P. O'BRIEN, Woburn, Massachusetts.

Machine for Treating Hides or Leather. U. S. Patent No. 1,053,297. A. H. KEHRHAHN, Frankfort Germany.

Tanning Composition and Process of Making the Same. U. S. Patent No. 1,053,798. A. G. ERNST, Junctiou City, Kansas. A method of producing a tanning composition which consists in combining malted barley, corn meal and ground rye chop with soft water, then thoroughly agitating the mixture and adding thereto compressed yeast, then allowing the mixture to stand until it has fermented and settled, then adding one quart of potato balls and one gallon of sumac berries, and then thoroughly commingling the ingredients. [The Editor suggests that this mixture should be salted to taste and taken with corned beef and cabbage.]

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CAESALPINIA DIGYNA.

By Thos. A. Faust.

Caesalpinia Digyna is a bush growing wild in Burmah, and yields tannin-bearing pods known commercially as Tari pods, and belonging to the same class as Divi Divi and Algarobilla. The plant is known in Burmah as Sun-le-the. The pods are dark brown in color, almost round, about three-fourths of an inch in diameter, and generally contain one or two large brown seeds. The pod cases are quite thin and contain practically all the tannin.

The *Chemical Engineer* for February, 1913 contains an article abstracted from the Calcutta Capital, which gives a very good description of the growth and characteristics of the plant, a part of which I will quote verbatim:

"These interesting pods, neglected now, are the product of a common wayside plant, a low growing, thorny scandent shrub which is wild in the hedgerows, waste lands and clearings near villages throughout the localities of its growth. Though it avoids situations that are flooded in the rains and usually thrives on fairly high land, it grows on the banks of rivers and forest streams and roadsides that skirt the feet of low hills. Though said to be found on the Eastern Himalaya, it is elsewhere essentially a low country plant. Its leaves, which are from six to nine inches in length, are freely divided like tamarind leaves; its racemes of flowers, in the axils of the leaves, appear in the middle of the southwest monsoons; and its pods, that are about two inches long, ripen in the months of April and May. For the highest purposes of their utilization, the pods should be gathered before they are ripe. When compared with their length, the pods are broad; but this dimension, though somewhat variable, seldom exceeds three-fourths of an inch. They are almost as thick as they are broad, with constrictions of the valves between the few seeds. The sutures, too, are remarkably thick and sinute at the constrictions between the seeds. The seeds themselves, about half an inch long, are nearly spherical in shape and dark greenish-brown in color. There are seldom more than three to the pod. They are sometimes roasted and eaten by children. The dried kernels contain from 25 to 27 per cent. of a thick pale yellow oil,

the composition, uses and value of which are at present but little known."

The *Madras Mail,* February 1900, contained an article on this material, which I believe was the first article of any importance published. In this article the material is reported to grow in abundance in Burmah, and is said to contain about 33 per cent. of tannic acid, although values of 50 or 60 per cent. are given which are no doubt too high, due to the rather imperfect method of tannin determination existing at that time.

A sample of this material was tried out at this time and the claim was made that it compared very favorably with the best Divi Divi, having the advantage of a larger percentage of tannin, and also it did not undergo any injurious fermentation.

The *Shoe and Leather Weekly* recently published an article abridged from the *Bulletin of the Imperial Institute,* which gives some interesting information on this material. The Officiating Reporter on Economic Products at Calcutta investigated the matter in 1893, and analyses made from these samples and also from some obtained a few years later, ran from 45 to 60 per cent. tannin. No very definite information on price or quantity available could be obtained. One tannery tried out 600 pounds of this material and gave a very favorable report.

Professor Procter in his "Principles of Leather Manufacture" states: "Caesalpinia Digyna promises to become a valuable tanning material. It has been introduced into England under the name of "white tan," which yields a leather quite as white as sumac; but the supply seems at present uncertain."

F. Austin Blockey in an article on "The Analysis of some New Tanning Materials" in the *Journal of the Society of Chemical Industry,* 1902, page 160, states that a sample examined showed 55 per cent. of tannin, and produced a leather equal in color to the best sumac. He believes the material to be of considerable value in the tanning industry.

The general consensus of the literature published shows the principal objection to the material to be the difficulty of obtaining it in the quantity sufficient for exportation. It is claimed, however, that the cultivation of this material is very easy. and that if the matter were undertaken, it would no doubt be successful. I

believe the Imperial Institute has under consideration at present the experimental cultivation of this plant.

As stated above, this material has been tried out by a few tanners in England, and several chemists abroad have done more or less work with it, but I do not believe that anything has been done with it in this country. I obtained a small sample from a New York importer, and made the analyses set down in the following table:

TABLE I.

	Analysis No. 1 Entire pods per cent.	Analysis No. 2 Pod cases per cent.
Moisture	7.82	7.12
Total extract	59.98	63.43
Soluble solids	57.21	61.05
Insolubles	2.77	2.38
Non-tannins	19.89	18.46
Tannin	37.32	42.59

For analysis No. 1, the entire pods were ground fine, and for analysis No. 2, the pods were crushed, the beans picked out, and the remaining pod cases ground fine and analyzed. The tannin in this latter sample, 42.59 per cent. on a 63.43 per cent. total solid basis, is very high. Color tests on sheepskin were made with both solutions, the former not being uniform in color, due no doubt to the oil in the beans, but the latter was a light uniform color.

These analyses were so promising that I asked the New York importer to get me a larger sample. Accordingly, he obtained about 200 pounds of this material, and I then carried out some additional experimental work in order to determine its tanning value as far as could be done in a laboratory, and also to get a better idea of the actual percentage of tannin found and the characteristics of this tannin. The following experiments were carried out:

Fifteen hundred grams. were ground roughly, and a rough separation was made of the dust, fibrous matter and beans. The dust constituted 46.16 per cent. of the whole, and on analysis showed 46.59 per cent. of tannin. A small piece of sheepskin tanned with this dust gave a very nice light color, one probably a shade darker than the color obtained from Sicily sumac.

After screening out the dust, the beans were picked out, and found to constitute 16.15 per cent. of the entire pod, and on analysis showed 10.32 per cent. of tannin. The fibrous matter constituted 37.68 per cent. of the entire pod, and on analysis showed 18.58 per cent. of tannin.

Color tests were made on sheepskin with both the fibrous matter and the beans. The former color was a little darker than that obtained from the dust, but was a color somewhat analagous to oak bark but considerably lighter in shade. The latter was quite dark, and as in the previous experiment, was no doubt due to the oil in the beans.

The beans were extracted with petroleum ether and 2.56 per cent. of oil was found, but no work was done on the nature or constitution of this oil. The percentage of oil I found did not confirm the results of other investigators who claimed to have found 25 to 30 per cent. This may have been due to the fact that the pods I used for my experiments were no doubt at least one year old.

Below is a table giving the full analysis of the dust, beans and fibrous matter:

TABLE II.

	Analysis No. 3 Dust per cent.	Analysis No. 4 Beans per cent.	Analysis No. 5 Fibrous matter per cent.
Moisture	7.2	—	7.4
Total extract	71.29	33.56	36.64
Soluble solids	67.00	31.74	35.21
Insolubles	4.29	1.82	1.43
Non-tannins	20.42	21.42	16.64
Tannin	46.58	10.32	18.57

The separation of the pods into three divisions by grinding roughly was not satisfactory, in that some of the beans were split, and influenced the percentage of fibrous matter, and the tannin found therein, the color also being darkened.

To get the matter on a more practical basis, the following experiment was carried out:

Two hundred grams. were taken and broken up roughly in a mortar and the beans removed by hand, showing a yield of 28½ per cent. of beans and 71½ per cent. of husks and dust. The analy-

sis of the ground pod cases showed 40.07 per cent. tannin and a color test made with this material gave a beautiful light color, one comparing very favorably with sumac. Experiments were made with this color test in order to determine the effect of light upon the color, and after four weeks it was found that the light had but a very slight darkening effect upon the color of the skin tanned with this material. This appears to me to be a distinct advantage of this material, in that skins tanned with other materials allied to the Tari pod, become very dark on exposure to light.

The full analysis of the ground pod cases is here given; this analysis being practically a duplicate of analysis No. 2:

TABLE III.

	Analysis No. 6 Pod cases per cent.
Moisture	7.00
Total extract	62.22
Soluble solids	58.75
Insolubles	3.47
Non-tannins	18.68
Tannin	40.07

I made a few tests with various reagents, and found that the behavior of this tannin was very similar to Divi Divi. Ferric alum produced a blue-black coloration, and bromine water gave no precipitate, thus indicating it to be a pyrogallol tannin. Lime water gave a dark yellow precipitate.

From the above analyses, it appears that this material should be of considerable value. I do not think it practical, however, for the tanner to separate the beans, but do believe that the pods could be leached whole very profitably, as the pod cases would leach out readily, and the oil in the bean would not be removed, so that the extracted solution should give a color as light as I obtained on the skin tanned with the liquor used for analysis No. 6.

The importer who furnished me with the samples used in these experiments informed me that this material could be bought for about $45.00 per short ton. This price compares very favorably with the price of other materials of the same tannin strength.

A NEW METHOD OF PREPARING SKINS FOR COLOR TESTING.

By Philip McCutcheon Armstrong.

In the report of the proceedings of the last meeting I see that Mr. Faust briefly mentioned my idea for preparing skins for color testing, and since the cat has shown her whiskers out of the bag I have decided to outline the process, so that the committee may try it out, although I feel that it is not yet perfected.

Last summer I spoke to Mr. Yocum of a curious fact which I had observed in the laboratory, namely that a piece of skin, which had been dehydrated with alcohol in the manner described by Knapp, would take up tanning matter at an amazing rate. He suggested that this might be worked up into a method of color testing, and I did considerable work on it during the fall and winter, with the result that, while the method is far from perfect as yet, it is a great improvement over the old method. If the process of preparing the skivers is carried out carefully, the results are absolutely uniform, and the color obtained is exactly that which would be obtained by tanning leather in the yard with the material tested. I made a color test on the yard liquors at our tannery (Armstrong Tanning Co., Detroit), and found that the color test showed exactly the shade of our tanned leather, before it was stuffed. Another advantage, in my opinion a minor one, is that a color test can be made in as short a time as *ten minutes,* although better results are obtained by prolonging the tanning.

In preparing the skivers, proceed as follows:

Take the skin directly from the lime, cut it into pieces of the desired size for the tests, and put it into a wide-mouth round-bottom flask, in which has been made up a solution of pure Ammonium Chloride, one-tenth of one per cent. This solution should be alkaline to methyl red, but not to phenolphthalein. Use plenty of solution, at least a liter for every square foot of skin. Shake vigorously occasionally, and test once in a while with phenolphthalein in a test tube. If the slightest redness appears, add a few drops of dilute hydrochloric acid, but not enough to make the solution more than faintly acid to methyl red. Start

in the morning, and then let it stand over night. Pour off the solution, and rinse rapidly three or four times with warm water (about 90 degrees F.). Fill the flask half full of warm water, and shake vigorously. Let it stand an hour and test the water for chlorides with silver nitrate. If there is a test, take fresh warm water, and let it stand another hour after shaking. Repeat until the water gives no test for chlorides. Two or three changes should suffice. Drain off the water, and place the skivers in another flask containing alcohol. The first time new alcohol must be used, but it can be kept and used again for the first wash. The skivers must be completely covered by the alcohol. Shake vigorously occasionally, and let stand over night. Then pour off the alcohol, and take fresh alcohol. This time the alcohol must always be new. Shake as before, and let stand over night again. Pour off the alcohol, and cover the skivers with ether. Shake, and let stand over night, pour off and repeat. The skins are now ready for color testing.

If the process has been carefully carried out, the result will be a perfectly neutral piece of skin, entirely dehydrated and free from inorganic matter. These skivers may be kept in ether as long as desired, or may be dried out in an exhausted dessicator, and kept in a sealed receptacle, but must be soaked up again in ether before using.

If it is necessary to use pickled skins, they must be made alkaline by soaking in *very* dilute sodium hydroxide solution, so that they are alkaline clear through before applying the ammonium chloride. It is better, however, to take the skins directly from the lime.

Methyl alcohol may be substituted for alcohol if desired. I cannot see any difference in the result.

To make the color test:

Take a ten degree liquor and warm it to 110 degrees F. and place a skiver in it directly from the ether. The warmth of the liquor will evaporate the ether, and cause a vacuum in the skin which will draw the liquor into the grain. A tanning action will be shown in a few seconds, and in ten or fifteen minutes the skiver will be tanned on the grain. If it is desired to tan the skiver through, a longer time must be taken. Rinse the skiver

in warm water, oil lightly on the grain with cod oil, and tack on a board to dry.

I do not recommend the adoption of this method exactly as it is outlined in this paper, but believe that if it is given to committee to try out, improvements will result, which will give us a method of color testing far superior to our present method. I would be glad to furnish pieces of skin prepared in this way to any of the committee who would like to try it, and help them in any way I can.

NOTE ON THE ANALYSIS OF TANNINS, III.

By Louis E. Levi and Aug. C. Orthmann.

The previous papers on the analysis of tannins (this JOURNAL, October, 1911, page 465 and January 1913, page 40) give some of the results obtained by us with the new method and also the observation that the sulphite-cellulose liquors are non-reactive.

This article is a continuation of the quantitative tests of different extracts and mixtures as compared with the hide powder method. It is also to be noted that interesting results have been obtained, in mixtures of tanning materials and the sulphite-cellulose liquors with the hide powder method as well as the new method.

TABLE I.

Extract	Insolubles	Hide powder method. Matter absorbed by hide powder	Reagent No. 33 tannin
Chestnut	0.77	27.48	26.91
Treated quebracho	1.08	35.18	35.04
Sumac	2.58	21.82	28.33
Hemlock	5.08	24.61	19.68
Myrobalan	3.78	26.68	24.59
Valonia	2.38	30.15	31.15
Ordinary quebracho	5.38	28.88	26.67
Mangrove	1.87	31.45	29.28
Sulphite-cellulose A	0.30	20.08	5.00
Sulphite-cellulose B	0.30	19.60	0.00

The following extracts were used for making mixtures: chestnut, treated quebracho, sumac, hemlock, myrobalan, valonia, ordinary quebracho, mangrove, sulphite-cellulose A and sulphite

cellulose B. The last two are ordinary products found in the market. They are hereafter designated simply as A and B. The analyses of the above materials are given in Table I. All figures are percentages. The hide powder analyses were made by the official method of the A. L. C. A.

Sixty-three mixtures of the above tanning materials were made, numbers 1 to 45 inclusive being weighed on a rough balance in large amounts so as to get as near to the commercial method of mixing as possible. Numbers 46 to 63 inclusive were weighed on the analytical balance. In Table II are given the analyses of these mixtures. Proportions in the mixtures are given in percentages, and the following abbreviations are used: ch = chestnut; tq = treated quebracho; s = sumac; h = hemlock; my = myrobalan; v = valonia; oq = ordinary quebracho; A and B, two sulphite-cellulose extracts.

TABLE II.

Mixture		Insolubles		Matter absorbed by hide powder		Tannin by reagent No. 33	
No.	Composition, per cent.	Found	Calc.	Found	Calc.	Found	Calc.
1.	50 ch, 50 A	0.41	0.54	21.67	23.78	13.81	15.91
2.	70 ch, 30 A	0.61	0.63	24.85	25.26	19.88	20.34
3.	90 ch, 10 A	0.79	0.72	27.53	26.74	26.74	24.72
4.	50 ch, 50 B	7.89	0.54	18.98	23.54	6.83	13.46
5.	70 ch, 30 B	4.32	0.63	22.74	25.12	15.15	18.84
6.	90 ch, 10 B	1.22	0.72	26.63	26.69	25.28	24.22
7.	50 ch, 25 A, 25 B	0.40	0.53	24.93	23.66	15.00	14.71
8.	70 ch, 15 A, 15 B	0.58	0.63	25.86	25.18	20.32	19.59
9.	90 ch, 5 A, 5 B	0.65	0.72	28.06	26.72	25.89	24.47
10.	50 tq, 50 A	0.52	0.69	24.24	27.63	18.36	20.02
11.	70 tq, 30 A	0.76	0.85	28.67	30.65	25.15	26.03
12.	90 tq, 10 A	1.07	1.00	33.48	33.67	32.84	32.04
13.	50 tq, 50 B	4.20	0.69	25.23	27.39	18.13	17.52
14.	70 tq, 30 B	3.11	0.85	29.10	30.51	25.89	24.53
15.	90 tq, 10 B	2.24	1.00	33.56	33.62	32.22	31.54
16.	50 tq, 25 A, 25 B	0.89	0.69	27.21	27.51	18.17	18.77
17.	70 tq, 15 A, 15 B	1.02	0.85	30.22	30.58	25.70	25.28
18.	90 tq, 5 A, 5 B	2.16	1.00	35.19	33.64	32.97	31.79
19.	50 s, 50 A	1.03	1.44	22.25	20.95	14.73	16.67
20.	70 s, 30 A	1.08	1.90	23.60	21.30	19.06	21.33
21.	90 s, 10 A	3.89	2.35	21.89	21.65	20.50	26.00
22.	50 s, 50 B	7.26	1.44	19.22	20.71	7.35	14.17
23.	70 s, 30 B	5.24	1.90	19.17	21.15	13.02	19.83
24.	90 s, 10 B	3.91	2.35	20.59	21.60	19.95	25.50

TABLE II.—(*Continued.*)

Mixture		Insolubles		Matter absorbed by hide powder		Tannin by reagent No. 33	
No.	Composition, per cent.	Found	Calc.	Found	Calc.	Found	Calc.
25.	50 s, 25 A, 25 B......	1.07	1.44	21.52	20.83	13.80	15.42
26.	70 s, 15 A, 15 B......	2.32	1.90	21.65	21.23	16.74	20.58
27.	90 s, 5 A, 5 B......	3.30	2.35	22.16	21.62	19.74	25.75
28.	50 h, 50 A............	0.14	2.69	?	22.35	13.90	12.34
29.	70 h, 30 A............	0.60	3.65	?	23.25	17.63	15.28
30.	90 h, 10 A............	7.36	4.60	20.41	24.16	17.32	18.21
31.	50 h, 50 B............	8.83	2.69	18.90	22.11	7.95	9.84
32.	70 h, 30 B............	9.03	3.65	18.34	23.11	11.77	13.78
33.	90 h, 10 B............	6.61	4.60	20.26	24.11	16.67	17.71
34.	50 h, 25 A, 25 B......	1.24	2.69	24.18	22.23	13.06	11.09
35.	70 h, 15 A, 15 B......	1.66	3.65	21.72	23.18	16.08	14.53
36.	90 h, 5 A, 5 B......	6.07	4.60	24.30	24.13	17.08	17.96
37.	50 my, 50 A............	1.46	2.04	23.83	23.38	14.61	14.80
38.	70 my, 30 A............	3.04	2.74	24.76	24.70	18.20	18.71
39.	90 my, 10 A............	4.13	3.43	25.94	26.02	21.97	22.63
40.	50 my, 50 B............	6.89	2.04	22.39	23.14	8.85	12.30
41.	70 my, 30 B............	7.59	2.74	23.31	24.56	14.60	17.21
42.	90 my, 10 B............	5.94	3.43	25.65	25.97	21.73	22.13
43.	50 my, 25 A, 25 B......	1.75	2.04	24.37	23.26	13.89	13.55
44.	70 my, 15 A, 15 B......	2.77	2.74	24.52	24.63	17.69	17.96
45.	90 my, 5 A, 5 B......	3.62	3.43	27.41	26.00	22.04	22.38
46.	46.25 v, 53.75 A........	0.72	1.26	27.57	24.74	15.06	17.09
47.	69.6 v, 30.4 A........	1.41	1.75	28.99	27.09	21.01	23.20
48.	46.5 v, 53.5 B........	7.05	1.27	21.47	24.51	6.56	14.48
49.	66.45 v, 33.55 B........	4.61	1.68	25.68	26.61	17.06	20.70
50.	45.33 v, 33.81 B, 20.86 A	4.11	1.24	25.13	24.48	11.13	15.16
51.	66.87 v, 16.38 B, 16.75 A	2.54	1.69	28.10	26.74	20.67	21.67
52.	51.69 oq, 48.31 A........	1.14	2.93	25.39	24.63	15.81	16.20
53.	66.52 oq, 33.48 A........	2.34	3.68	26.19	25.93	19.26	19.41
54.	49.28 oq, 50.72 B........	6.01	2.80	21.19	24.17	11.25	13.14
55.	66.04 oq, 33.96 B........	6.66	3.65	23.60	25.73	15.60	17.61
56.	47.85 oq, 26.33 B, 25.82 A	2.46	2.73	23.27	24.16	13.90	14.05
57.	63.69 oq, 17.65 B, 18.66 A	3.56	3.54	24.48	25.60	17.01	17.92
58.	52.62 ma, 47.38 A.......	0.29	1.13	20.41	26.03	16.24	17.79
59.	68.3 ma, 31.7 A.......	0.59	1.37	23.55	27.85	19.69	21.58
60.	46.1 ma, 53.9 B.......	2.15	1.02	20.90	25.06	13.17	13.50
61.	64.4 ma, 35.6 B.......	2.00	1.31	23.80	27.33	17.10	18.86
62.	45.3 ma, 27.2 B, 27.5 A	1.24	1.01	21.59	25.10	13.61	14.64
63.	65.8 ma, 18 B, 16.2 A	1.00	1.33	25.53	17.48	18.85	20.08

Among the several sulphite-cellulose extracts A which have come to our notice, it was found that the actual tannin content

varied from zero to 5 per cent. We selected the one that contained 5 per cent. tannin for the above analyses.

The chromium content of the sulphite-cellulose extracts should also be taken into consideration as the chromium is liable to affect the result.

It is also to be borne in mind that these figures do not show the tanning properties of the sulphite-cellulose liquors as both A and B are absorbed by the hide powder in practically the same proportion, as shown by the above analyses.

As noted in our former article the quantitative results indicate clearly the amounts of sulphite-cellulose extracts in the mixtures, showing that reagent No. 33 does not act upon these extracts, giving the chemist a simple method for the detection of mixtures of sulphite-cellulose extracts in tanning extracts.

In our next paper we hope to give a general resumé of the work done towards a new method of tannin analysis, the preparation of the reagent No. 33 as well as an investigation of the formation of insolubles in mixtures of sulphite-cellulose extracts and tanning extracts.

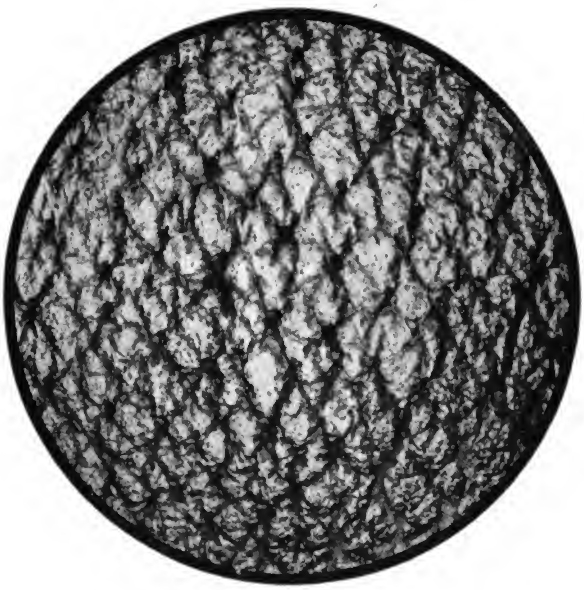
LABORATORY OF PFISTER AND VOGEL LEA. CO.,
March, 1913. Milwaukee, Wis.

INDENTIFICATION OF TANNED SKINS.[1]

By C. Frank Sammet,
Assistant Chemist, Leather and Paper Laboratory, Bureau of Chemistry, Department of Agriculture.

The identification of leathers, including the detection of imitations, is, perhaps, simple when we have the whole skin before us and can judge by its size, shape, markings, and grain the kind of animal from which it came, but in many instances it is desirable to identify small samples of leather, or leather which has been manufactured into various articles. For the latter cases, and for the use of inexperienced observers who would find such knowledge useful, the method herein described will greatly facilitate the identification.

[1] Paper read at the Ninth Annual Convention, *A. L. C. A.*, Washington, D. C., December 7, 1912.

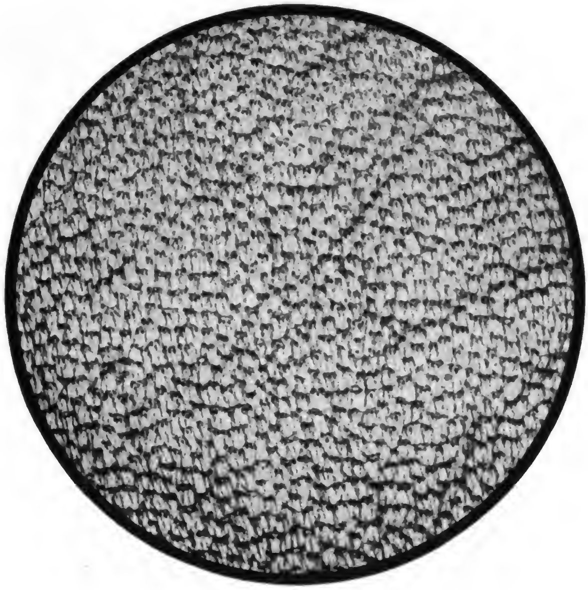


Pig Skin.

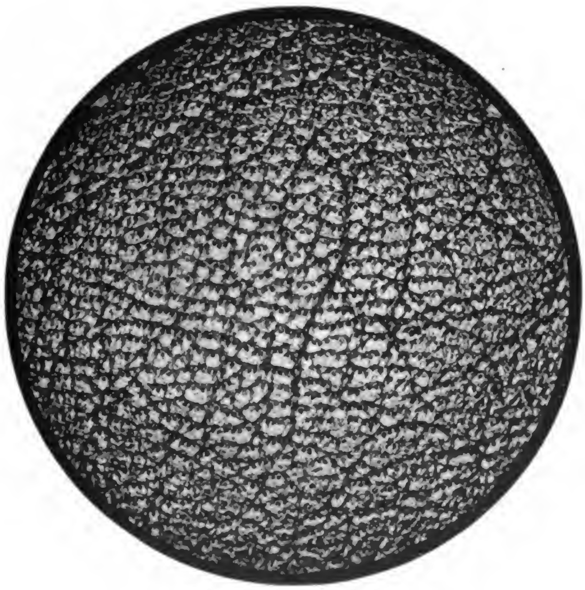
Imitation Pig Skin.
(On sheep.)

Calf Skin.

Cow Skin.

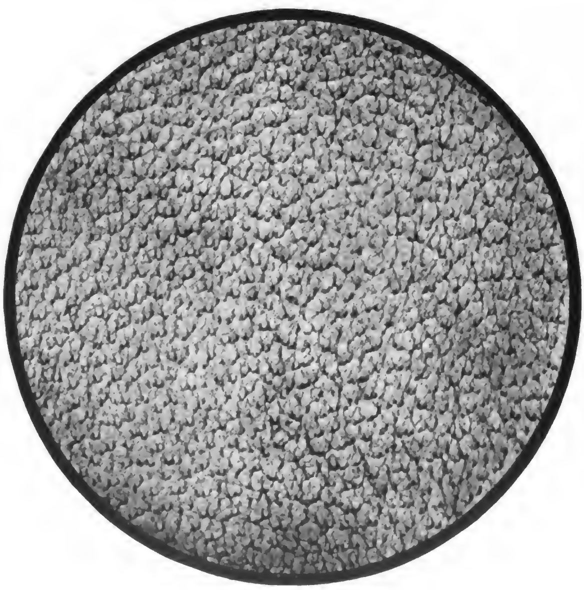


Goat Skin.
(In crust.)

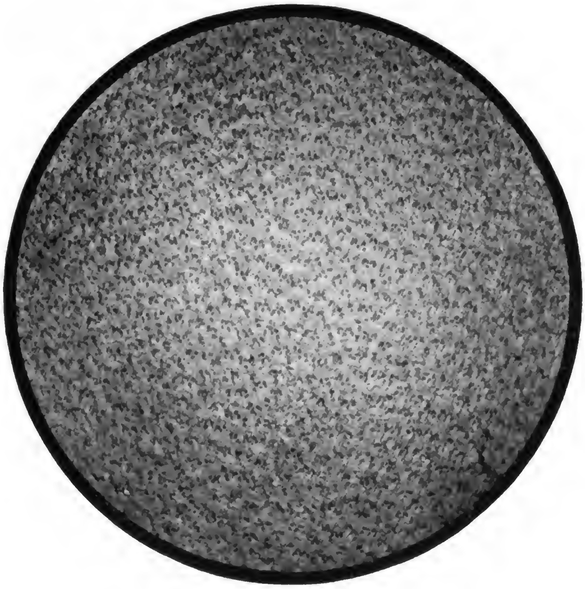


Goat Skin.
(Boarded.)

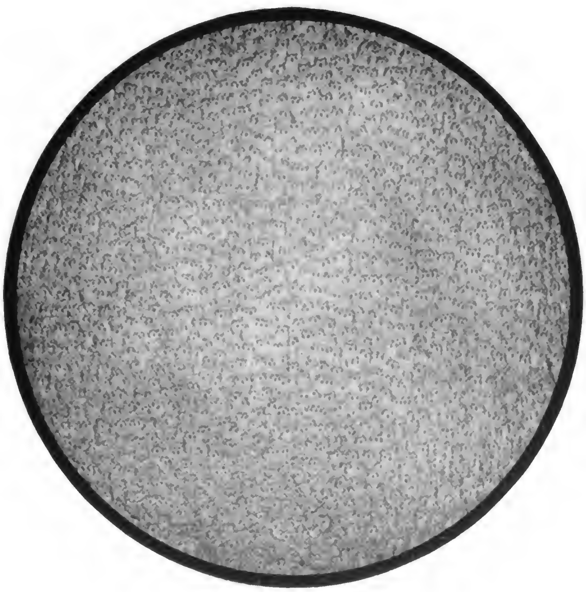
Sheep Skin.



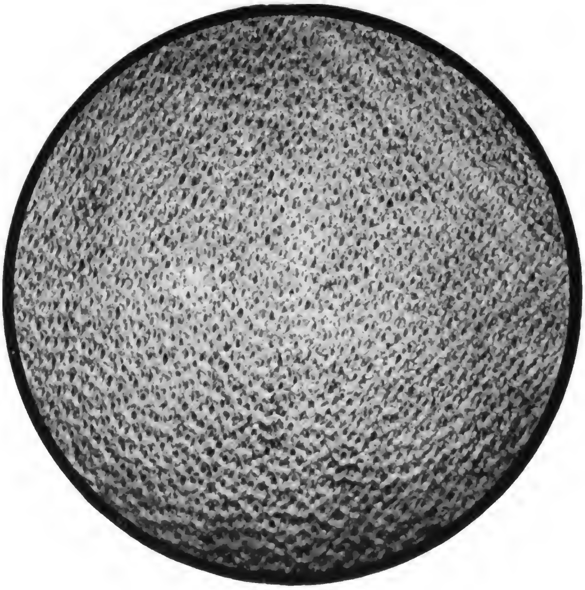
India Sheep Skin.



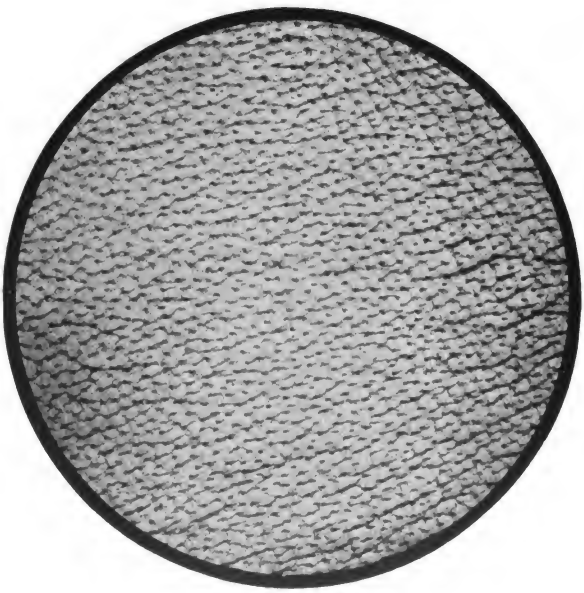
Lamb Skin.



Kid Skin.



Horse Skin.



Kangaroo Skin.
(Gray.)

It is difficult to examine the grain of leather under the magnifying glass and carry in mind a true impression of this grain for comparison with that of the genuine leather. The area under magnification is so small and the brilliant or black color of certain leathers so likely to influence the light and shade effects to the eye that the deep hair follicles which are the characteristic markings of the grain are obscured.

Photographs are a great convenience for making comparisons of grains of leathers, but heretofore the photographing of these grains has been attended with but little success, because of the difficulty of properly lighting the surface by reflected light. Contrast and detail were consequently lost in the photograph and identification was made uncertain. The photographs shown (see Plates), however, indicate the excellent detail obtained in this method, where a wax impression of the grain is made and this impression photographed in transmitted light under a magnification of 3¼ diameters.

A mixture of beeswax and paraffin is melted on a glass plate and allowed to flow uniformly over the surface. Paraffin alone has a rough surface when it hardens, but this condition is modified by the addition of the much finer grained beeswax, thus making the mixture more suitable for the photographing. Furthermore, beeswax imparts a certain tenacity to the cooling wax, which prevents it from stripping from the plate, yet permits a clean separation from the leather.

When the wax has cooled to almost a solid state, the leather should be stretched over a perfectly flat surface and pressed tightly down upon the wax and held thus for a few minutes until the latter has hardened. The leather is then easily separated from the wax, leaving a perfect impression of the grain upon the wax-coated glass. Care should be observed to take the impression just as the surface of the wax crystallizes, for if the wax is too hot it will be absorbed by the leather and if too cold a detailed impression can not be obtained. This impression is permanent enough to keep for future reference. It can be photographed in transmitted light and the reproduction thus obtained used as a standard for comparison. Sufficient contrast is obtained in the negative, as the transmitted light is greatly dispersed

in passing through the more raised portions of the crystalline wax, which represent the indentations of the grain, giving them depth and contrasting them with the high lights represented by the thin portions of the wax. A perfectly even film of the impression is essential, as the slightest variation in thickness produces an unevenness in the photograph. The thinner the film of wax the more striking is the embossed effect produced.

The procedure is valuable as a means of becoming familiar with the characteristic grains of leathers, and of having the reproductions of these grains in a convenient form as standards for comparison, which greatly facilitates the detection of imitations.

(This article has been published by the Department of Agriculture as circular 110, Bureau of Chemistry.)

ABSTRACTS.

Objections to the Use of Sodium Sulphate. ED. NIHOUL. *Conceria*, 20, 270. N. maintains that sodium sulphate is not as efficacious as common salt for salting hides and holds that it is absolutely useless when employed in small amounts. In view of the large amount in which it must be used, the opportunities for fraud on the part of the seller are considerable. Certain errors (due to unequal distribution of salt in the hide and to salt remaining in the hide when the latter is soaked in a known volume of water) occur in estimating an overcharge of salt by means of an analysis of a small sample of the hide; when the hide is overcharged with sulphate of soda in large amounts or with a mixture of this and salt, the detection and determination of this excess is still more difficult, even when such excess is suspected by the buyer. It should be noted that Glaubers salt ($Na_2SO_4.10H_2O$) loses its water of crystallization in calcination and is reduced to sodium sulphide by contact with the organic material of the hide; the sulphide, as determined in the ash, then represents only 24.22 per cent. of the original amount of Glaubers salt added. When calcined sulphate of soda has been used, another difficulty, due to the presence of free sulphuric acid, is encountered, since this free acid remains in the hide, regardless of the duration of the bath. It must not be forgotten, also, that anhydrous sulphate of soda is hygroscopic and that the weight of absorbed water is added to the weight of the hide.

H. S. PAINE.

Effects of Oils and Fats. ANON. *Conceria*, 20, 412-3. The effects of various oils and fats on leather are described. Cod liver oil fills the flesh and gives a good weight; under certain conditions it produces a dark-

brown color of poor appearance. Whale oil yields a good weight and produces a pale yellow color, but has a very bad effect on the flesh. Cottonseed oil is only used for grained leather; it gives a clear golden-yellow color and a good weight, but renders the leather rather dry. Rapeseed oil is also used for grained leather; it gives a clear golden-yellow color and a moderate weight, and also has a drying effect on the leather. Castor oil is well suited for grained leather; it gives a good weight, is without color, and has a pronounced softening action on the leather. Castor oil has the disadvantage of being gummy and also of expanding the leather, especially the flesh side; it is much used in fat-liquors, since it does not disturb the color and is as clear as other oils. Oil of sesame produces a light yellow color and is well suited for grained leather; it has the characteristic property of being assimilated by leather in large amount without the latter appearing oily. Olive oil does not produce weight and is only useful for grained leathers; it gives a pale yellow color. Bone oil is of value for grained leathers only and produces a light yellow color; it has a softening effect and gives a good weight. Linseed oil, used in the preparation of varnished leather and in the finishing of morocco leather, has been largely displaced for these purposes by mineral oil. Tallow yields a good weight and produces a light yellow color; it has a filling action and causes hardening, especially on the flesh side, when mixed with *dégras*. Spermaceti oil has the same action on leather as whale oil. Refined cottonseed oil produces considerable weight and gives a brown color; it expands the leather and tends to give it a gummy consistency. Mineral oil is useful for preventing fermentation and is best used in mixture with other oils; it does not have a drying action and is a good lubricant. Lanolin gives an unusually good weight; it produces a brown color and, because of its property of forming emulsions with water, is a good substitute for *dégras*. Japanese wax fills the pores and is therefore valuable for finishing. Mutton tallow gives less weight than beef tallow; it is without color, has a pronounced filling action, and is less oily than beef tallow. Lard gives a tolerably good weight; it is very penetrating and has a softening action on leather. Palm oil yields a good weight; it produces a golden-yellow color and is useful for correcting poor coloring. The necessity for further study of the action of oils on leather is urged. H. S. Paine.

Cassia Auriculata or Tarwar Bark: Its Analysis and Use. P. V. Mehd. *Year Book of Indian Guild of Sci. and Technol.*, 1912, 137-138. Infusions were prepared from the powdered bark at 30°-40° C., 40°-50° C., 50°-60° C., and 85°-90° C., respectively, and it was found that whilst the non-tannins (9.8-11.8 per cent.) were extracted almost completely even at the lower temperatures, the maximum amount of tannin (21.9-22.1 per cent.) was extracted at 85°-90° C. No glucose could be detected in the infusion. The precipitate produced with basic lead acetate was of a peculiar chocolate color which appears to be characteristic of cassia (tarwar) bark. A piece of English hide was tanned for three weeks in liquors, prepared

from myrobalans and cassia bark, which had stood for over two weeks; the acidity of the liquor was maintained by addition of formic acid, and the strength was kept up by addition of further quantities of the infusion of cassia bark and myrobalans. The hide was then drummed with a strong freshly prepared infusion of myrobalans to which myrobalans dust was added. After drumming for half an hour every day during one week, the leather was taken out and finished in the usual way, using cod oil and drying at 60°-70° F. (15.5-21° C.). The leather was of a very light color, possessed a mellow feel, and gave the following results on analysis: moisture, 12.5; oil, 2.0; water-soluble matter, 16.9; hide-substance, 40.4; combined tannin, 28.2; glucose, 0.0 per cent. It is concluded that though cassia bark may not be suitable for fancy leather goods and leather for book-binding, it may be used with advantage for heavy as well as for dressing leathers, giving when blended with myrobalans, a mellow tannage, and a very good, light-colored leather, which compares favorably with that produced by any of the other blends at present in common use.—A. S. in *J. S. C. I.*

Utilization of Residues from Chrome Tannage. DR. E. GIUSIANA. *Le Cuir,* Dec. 15, 1912, pp. 799-803. Spent liquors from two-bath tannage are passed through a fine screen into a wooden tank. The quantity of bichromate and of free chromic acid are determined by analysis, and the proper amount of sulphuric acid added to convert the bichromate into chromic acid. The whole is then reduced to basic chrome by passing sulphur dioxide through. The chrome is then precipitated by adding the calculated quantity of carbonate of soda. After settling, the liquid is drawn off, and the precipitate washed several times. In the case of one-bath liquors, the precipitation with soda is done at once, and the precipitate washed in the same manner. The precipitate is chromium hydroxide, and may be converted into the oxide by mild heat in an iron vessel. Scrap and refuse containing chrome are burned, and the ash added to the oxide from the liquor. The oxide is reconverted into chromate by heating with nitrate of soda, and the chromate into bichromate by treatment with sulphuric acid. L. B.

Tannery Effluents. Lecture by M. DUYCK, chemist to the Belgian minister of finance, before the Tanners' "Chambre syndicale" at Brussels. *La Halle aux Cuirs,* Feb. 9, 1913, p. t. 18-21. The lecturer dwells at some length on the Belgian laws relating to contamination of streams, and the general failure to enforce them. He enumerates the kinds of tannery wastes, and remarks that the problem of purification is difficult because the effluent from the same tannery varies from hour to hour and from day to day. Bacterial purification, applied so successfully to general sewage, is hindered or prevented by the chemicals carried by tannery wastes. The experience of Gloversville, N. Y., is cited. Conditions which should be fulfilled by effluent from bacterial purification plants are quoted from Dunbar: 1. No solids in suspension; 2. A sample kept in a stoppered

vessel for one week at 40° C. should develop no putrid odor and no hydrogen sulphide; 3. Fish must be able to live in the undiluted effluent; 4. The oxygen consumption must be diminished by from 60 to 65 per cent. After passing through a strainer to catch light particles, the waste may be held in settling tanks and treated with a coagulant to precipitate colloid substances, and with chloride of lime to deodorize and decolorize the water. Chloride of lime also kills bacteria, even the very resistant germs of anthrax and lock-jaw. After settling, the waters are decanted or filtered or both. The Vial decantation process permits the passage of well clarified effluent at the rate of 11 cubic yards daily per square yard of surface. The disposal of sludge is discussed, and it is stated that it is being burned at some installations. L. B.

Natural Organic Acids of Oakwood Extract. J. JEDLICKA. *Collegium*, Feb., 1913, No. 514, pp. 33-9. Freshly sawn green oak lumber with a water-content of about 40 per cent. smells strongly of acetic acid. Air-dry wood, with an average of 25 per cent. water is used for extract making and the smell is less strong. The vapors in the vacuum pans are strongly acid, as is shown by their action on the apparatus. The most important acid is acetic, mixed with which is found about one-twentieth as much formic. To estimate the volatile acid, the liquor from the diffusion apparatus was taken as it was, but extract was diluted to 3 or 4° Bé. In a large round flask 200 cc. were distilled under reduced pressure to 25 cc., more water added and the process repeated. Heat was applied by means of a paraffin bath. The distillate is titrated with N/10 NaOH and phenolphthalein. The result was verified by evaporating the neutralized solution to dryness, decomposing the salt with phosphoric acid and again titrating. In the later fractions of the distillate CO_2 is found. Furol is also present, due to the pentosans in the extract. From 200 cc. unconcentrated liquor, 8 successive distillates took the following quantities of N/10 NaOH (cc.), 42.5, 4.5, 3.0, 2.5, 2.0, 2.2, 2.0, 1.8, total 60.5 cc., = 0.363 g. acetic acid, = 0.18 per cent. The liquor contained 3.673 per cent. solids and 2.313 per cent. tannin. Under the actual conditions of extraction, the acetic acid content was from 2.5 to 5 per cent. of the whole extractive material. The finished extract of 25° Bé. gave from 0.6 to 1.3 per cent. acetic acid. The vapor from the evaporators is led through large copper washers, placed behind each evaporator and filled with milk of lime to remove acids from the vapor. Thus the extract contains only a portion of the acid originally extracted from the wood. The calcium acetate solution so obtained is filtered and evaporated, yielding a nearly white powder, whose average constitution is as follows: Calcium acetate 89 per cent., calcium formate 5 per cent., calcium carbonate 1 per cent., water (combined) 5 per cent. The product has a faint pleasant odor, resembling vanillin, due to a vanilla-like substance existing in the wood-cells. If the pulverized wood be shaken with ether and the solution evaporated, the residue gives with phloroglucin and concentrated HCl the well-known vanillin reaction. Acetic and formic acids were estimated by Fresenius

method, by distillation with phosphoric acid and titrating the distillate. Then the formic acid is separately estimated by reducing $HgCl_2$ to Hg_2Cl_2 and weighing the reduced salt. It is necessary to use a large excess of $HgCl_2$ and boil one hour. The boiling is done in an Erlenmeyer with long tube attached to avoid vaporization of the mercury salt. The combined water is driven out at from 150° to 250° C. It is hard to determine the point at which the water is all driven off, since not only formate-containing, but even pure acetate of lime begins to decompose into acetone and aldehyde at a lower temperature. The figure found for water (4 to 6 per cent.) agrees fairly well to ½ molecule of water of crystallization in calcium acetate, which would be 5.39 per cent. for the pure salt. In order to determine whether any acids of the series $C_nH_{2n}O_2$ having higher molecular weight than acetic acid were present, the author distilled 100 g. of the calcium acetate in 1 per cent. solution from phosphoric acid, collected the first 10 per cent. of distillate, converted it into the calcium salt and again distilled from phosphoric acid, collecting the first 10 per cent., which was thus 1 per cent. of the original quantity. It is well known that if a mixture of acids of this series be distilled, those having the highest molecular weights tend to go over first. If any propionic acid were present, it should be found in the 1 per cent. above mentioned. The acid was converted into the silver salt, and the proportion of silver found on analysis showed it to be acetic acid. The process above described for reclaiming acetic acid from the vapors yields from 20 to 25 kilos of acid per 100 quintals of wood (8 to 10 pounds per ton).

The author believes that much the largest part of the acetic acid in oakwood is present as alkaline salts of the acid, and that the acid is set free from these by the oak tannin. The conditions which determine the liberation of the acid are, (1) the relative concentration of acetate and tannin, (2) sufficient moisture and (3) favorable temperature. In freshly sawed wood, acetic acid is freed at ordinary temperatures, while only traces are observable in air-dry wood. In the extract and liquors, rise of temperature is necessary, and the presence of sufficient water. In the extract, plenty of alkali and alkaline earths are present to combine with all the acetic acid, but some acid is nevertheless present in the free state, which may be obtained, together with gallic acid and some other bodies, by shaking out with ether. The ether extract, which smells strongly of acetic acid, is evaporated, taken up in water, phosphoric acid added, and the whole distilled. The acetic acid is titrated in the filtrate. By this means from 0.2 to 0.3 per cent. acetic acid were found in oak-wood extract of 25° Bé. Both oak tannin and gall tannin decompose other acetates, and also carbonates at 100° C. Volatile acids are produced also in the manufacture of other wood extracts. Wäntig uses the volatile acids of quebracho in clarifying his extract. Kerr and Wilson (this JOURNAL, VII, pp. 77-87) found 0.08 per cent. acetic acid in chestnut liquors, and in reply to the suggestion that the acid was produced in the process of distillation, described an experiment which seemed to show that it was not so pro-

duced. The author agrees with this opinion of Kerr and Wilson, and also with their opinion that a considerable decomposition of tannin takes place in the manufacture of extract. During concentration, of the leach-house liquor to extract in the most modern high vacuum evaporators, the "tannin quotient" (parts tannin to 100 parts total solids) falls 2 or 3 points, *e.g.*, from 60 to 58. The author believes that gallic acid is formed, but the quantitative estimation of the latter is rendered difficult by the fact that in shaking out the extract with ether an emulsion forms which is difficult to break. The use of alcohol to break the emulsion carries other substances into solution. The color reactions with potassium cyanide, barium hydroxide, sodium arsenate, etc., are also liable to error because of the presence of an ether-soluble substance which rapidly oxidizes in the air, producing a cherry-red color. This body (which is also present in chestnut wood) has been observed by Böttinger (Liebig's *Annalen*, Vol. 263).

In common with many other plants, oakwood contains calcium oxalate, and some of this passes into the liquors and is deposited on the pans, forming a troublesome scale. Most of the oxalate is present in suspension in the extract. The sediment when washed and dried yields 35-40 per cent. of ash. Of this, 6.5 per cent. is insoluble in nitric acid, 36.7 per cent. is lead oxide, 31.7 per cent. lime, 4.5 per cent. phosphorus pentoxide and 20.3 per cent. carbon dioxide. The dry sediment had in this case about 19.8 per cent. oxalic acid. About half of the sediment is organic matter only slightly soluble in hot water, the analyzed portion giving the following calculated percentages on the dry total sediment: lead oxalate, 20 per cent.; calcium oxalate, 22.9 per cent.; tri-calcium phosphate, 2.4 per cent.; excess lime, 2.7 per cent.; insoluble, 2.5 per cent. Other samples showed from 18 to 21 per cent. oxalic acid, determined by long boiling with soda, filtering, saturating with acetic acid, and precipitating with calcium chloride. One hundred pounds of wood with 25 per cent. water gave on the freshly extracted liquor 0.03 to 0.04 pound oxalic acid as oxalate. In the finished extract only traces were present.

It is surprising that the vapors which have passed through the milk of lime in the washers should contain carbon dioxide, but many analyses show an average of 0.9 per cent. by volume of CO_2 in the air passing through the vacuum pump, amounting to 528 pounds of carbon dioxide in 24 hours. One-sixth of this was due to the leach water. Another part is from colloidal calcium carbonate present in the oakwood, and another to the partial decomposition of tannin at the boiling point. The last fact was proved by the author by boiling diluted extract under a reflux condenser for half a day, the flask being connected to receivers containing baryta water, through which was drawn a current of air free of CO_2. The baryta water was then removed and titrated, and fresh substituted. The process was repeated 42 times, and the diluted extract continued to yield CO_2. About 1 per cent. of CO_2 altogether was collected, and the tannin quotient fell from 59 to 50.

L. B.

Some Products Obtained by Reducing Ellagic Acid. M. NIERENSTEIN and F. W. RIXON. *Collegium*, No. 514, 1913, p. 53. The reduction of digallic acid to leucodigallic acid has been described (*Collegium*, 1912, p. 202; this J., VII, p. 579). The authors have by electrolytic methods reduced ellagic acid at different temperatures. At room temperature leucoellagic acid was produced. This body is colorless, in contrast to ellagic acid which is a coloring matter. This contrast suggests that between digallic acid (tannin) and leucodigallic acid, which has no tanning properties. At 70° C. the product of reduction is pentaoxybiphenylmethylolid, and at 110° a series of hexaoxydiphenyls. From leucoellagic acid, leucoellagdicarbonic acid was obtained, and split into optically active components. The apparatus employed had a mercury kathode and a nickel anode, with a porous ware cell. The curent employed was 2.5 amperes, the ellagic acid being partly dissolved and partly suspended in a 4N solution of NaOH. L. B.

Oropon Bates. W. EITNER. *Gerber*, 1912 [38], 311-3. The results of experiments made upon a new brand of Oropon "EC" are given. It resembles the old form "S," being a yellow powder consisting of powdered straw saturated with an extract of the pancreatic gland from cattle. Of the pancreatic substances contained in Oropon, the trypsin dissolves the albumen of the hide and loosens the fiber, while another component acts upon the fatty matters. In addition, Oropon contains substances like sal-ammoniac which are effective in de-liming without use of acids. The earlier Oropon "S" was intended to replace dog-dung bate in which it has proved successful while avoiding the undesirable fermentations liable in puering. In removal of the fatty scum, Oropon is superior, the ordinary dung bate having only a loosening effect requiring mechanical aid with risk of injury to the grain. A "digestive" bate, like Oropon, has a further merit in operating at moderate temperature (25°) if sufficient time be allowed. There is not the same danger in prolonging the time as with dung bates which from caution are sometimes too short to make soft leather. Oropon bates, especially the EC brand, can be extended for days. Even an overbated leather showed after 8 days sound inner fiber, the soft parts only having been removed.

The author experimented with bates of 500 gms. Oropon EC to 100 kilos pelt at temperatures from 18 to 34° C., 14 hours to 4 days. Cattle and swine hides from the limes, after merely watering without acid treatment, were bated and came out completely fallen down, with smooth fine grain, easily cleaned. The tannage gave a mild, full leather.

That intended for dyeing (pigskin) had a spotless grain which absorbed the color thoroughly. Argentine lambskins and Asiatic sheepskins were easily cleaned from fat after an Oropon bate and gave good chrome leather. In conclusion, Oropon S is a suitable puer substitute for glacé and kid while for leathers which require a pigeon dung bate, Oropon EC is used. W. J. K.

Lowering the Loss by Washing in Certain Leathers. W. Eitner. *Gerber,* 1913 [39], 1-3. The line between natural rendement and loading is not precise. Reclamations are often based on the results of an analysis of a normally made, deserving leather. With the rest, soluble non-tans are often legitimately present and swell the analytical count against the leather.

To overcome this unfair valuation a device is used for fixing the tannin, which consists in the application of glue. It is especially applicable to leathers which have been filled with tan-stuff in the drum, or those which after tannage have received a treatment in vats or even lay-aways and pits with warm concentrated liquors. After draining and partially drying and pressing, the leather is milled to loosen it, then piled for 24 hours to equalize the distribution of the moisture and finally brushed with or dipped in the glue solution, finishing with the drum. After lying 24 hours, the leather can be washed without loss, or may receive an after-tannage for bleaching, with sumach, myrobalans or gambier. Excess of glue on the surface darkens the leather and should be washed out or fixed with the above light-colored tans. Leathers which contain no large excess of tannin, after drumming with glue, are treated with a tan-stuff, best a good grade of extract like Triumph, mixed with chestnut if desired. Muddy extracts (Argentine) are risky and give miscolored, spotted leather. Good grade Cologne glue is used and will absorb its own weight of water without flowing. The swollen glue is melted on the water-bath and 10 per cent. (dry glue = 100) of butyric or lactic acid added, left stand 12 hours and finally diluted with 2 parts water. For dry, extract-filled leather, 2.5 to 3.5 per cent. dry glue is required, for others, 2 per cent. The object of the above treatment is not to secure increase in weight but in good quality. Unfixed tans give brittle leather, hard to curry in the machine and impossible for hammering; this defect is most marked with Argentine extract and cannot be remedied with glue. Normally, the glue tannin precipitate is elastic and fills out the looser parts of the leather. Only the better sorts of tan-stuffs are suited for combination with glue. Sulphite cellulose lye is not fixed at all and in general leather is made worse by applying glue in presence of foreign loading materials.

Chrome salts also fix glue which can therefore be applied to chrome sole leather, the process being similar to that for vegetable tanned leather. The patent processes for treatment with glue before or during chrome tannage are worthless. W. J. K.

Reptile Leather and Imitations. W. Eitner. *Gerber* 1913 [39], 15-17. Crocodile, lizard, serpent skins, etc., form a considerable item in commerce, being fashionable and durable and are much imitated. The skins of all armored and scaled reptiles are hard to soften and putrefy very easily, hence the soaking is difficult. The soaks are sharpened with 10 per cent. sod. sulphide for alligator, 5 per cent. for lizard or serpent (skin = 100); the scales become loose and can be removed in a few days.

A lime sharpened with arsenic or calcin follows, serving only to loosen the hide which is important because of the unusually dense texture of the fiber. For alligator, 3 weeks liming are needed, for lizard, 2. A dung bate followed by bran is used for alligator while a bran bate alone is sufficient for lizard. Sumac or gambier are used for tanning, finishing in warm liquors. Serpent skins are more sensitive and only cold liquors are used. Frogskin leather comes from Japan, vegetable tanned; the skins reach 13 cm. length and the marking is prized. Reptile leather is curried but once on the grain, since this characterizes the leather and the natural markings give it its value.

The scarcity and cost of the genuine material have made its imitations numerous and these have reached a perfection which sometimes deceives the tradesman himself. They do not, however, reach the durability of the genuine leather. Leathers intended for lizard or serpent skins are left in the natural color, others are suitably dyed. The most important part of the manufacture is the production of the imitation grain in machine presses fitted with galvanic casts transferred from the natural skin. The second dyeing requires care, the dye being locally rubbed in with pads. The natural markings are imitated by stencilling; a 5 per cent. solution of iron acetate or alum is used for lizard, aniline colors for serpent and frog markings. The fine rings and dots of lizard marking are too small for stencilling and processes are used similar to those used in printing textiles. In the first method (Reservage) an emulsion of soap, fat and wax is printed and the color is afterwards fixed only on the ungreased surface, leaving a light design on a dark ground. This process is also used for antique leather, the elevations receiving the emulsion and the depressions retaining the color. A better process is padding (Enlevage). A discharge of 10 parts salt of sorrel, 3 parts dextrin in 100 parts water is printed onto iron black, sharply bleaching out the marking in very deceptive imitation. Egg albumen glaze is applied and machined, requiring care. The crocodile hornback gives more satisfaction left matt without lacquer. Serpent skin requires delicate hand work in glazing. W. J. K.

Anthrax Disinfection of Hides. JOSEF SCHNURER and FRANZ SEVCIK. *Tierärztliches Zentralbl.* through *Gerber,* 1913 [39], 17-18. One of the authors (Sch.) had earlier found that Seymour-Jones' disinfecting liquid of 1 per cent. formic acid, 0.02 per cent. sublimate applied for 24 hours was efficient. On now repeating these experiments with the exception that the test piece was first soaked 2 hours in 1 per cent. sterile sod. sulphide to remove excess of sublimate, the cultures developed anthrax while an untreated test remained sterile. This showed that the sterilization in the culture was due to retained sublimate. Further research demonstrated that to free heavy hides from anthrax spores in 24 hours, a concentration of 0.2 per cent. sublimate, 1 per cent. formic acid was needful, either at room temperature or at 6-10° C. Hides thus treated were found by Dr. W. Eitner not to have suffered for tanning purposes.

Trials of Schattenfroh's pickling method with 2 per cent. HCl, 10 per cent. NaCl after 72 hours action still showed infection in 4 tests out of 11 with thick cattle hide. Schattenfroh's favorable results were probably due to the thinness of the skins (lamb, sheep, goat) employed. A test with Seymour-Jones' disinfectant on an infected heavy sheepskin was sterile after first degreasing with petroleum ether, but if this be omitted it is necessary to use a ten-fold concentration. W. J. K.

Cellulose Extract. W. EITNER. *Gerber,* 1913 [39], 43-4, 57-9. This substance still seems to have credit in some directions as a tanning material. The author finds Lepetit's designation of "pseudotannin" well suited, its virtue being a mere semblance (Schein). That it is absorbed by hide powder leads many chemists to rate it as tannin, or tanning substance. It appears also to the practical tanner to give something like leather but experience shows that alone it renders no real leather and is useful only in combination with genuine tan-stuffs. In sole leather manufacture it was found capable of increasing the rendement and to escape classification by the analyst with the loading materials of the starch type. As an adulterant of vegetable tanning agents, cellulose extract is appreciated in its true character. Commenting on Dr. Parker's suggestion in the London Congress that cellulose extract, being a novelty, must like quebracho, mangrove and mallet in their day, first be tried out, the author repeats that it is not a tan-stuff and is more comparable with vegetable dyes.

Its use as an adulterant of extracts has attained great dimensions, especially abroad. This is more at the hands of dealers than manufacturers, who might discredit their products. This blending is not only for cheapening but also to improve the appearance of thick, inferior quebracho extracts by thinning and lightening. Chestnut extract, being of similar appearance, is also adulterated with cellulose extract and even substituted by it, with addition of myrobalans, quebracho and mangrove. Cellulose extract may be identified and roughly estimated by several methods. The ratio of non-tans to tans (author's designation, substances unabsorbed and absorbed by hide powder) is characteristic. He found for Kronstadt and Westphalian extracts a ratio of 1 : 0.82, which differs from any vegetable tanning materials, they ranging from 1 : 10 (quebracho) to 1 : 2.3 (oakwood). Still more characteristic is the low value found for the "tans" by Löwenthal's oxidation with permanganate, it being but one-sixth that given by hide powder (Sody); this difference is much less with other extracts. In this respect, cellulose resembles sulphited extracts which give low Löwenthal numbers. The high ash (sometimes 9 per cent.) also characterizes cellulose. The high content of non-tans has no commercial value; these do not ferment or produce acid as sometimes claimed.

The commendations of cellulose come more from theorists than as reports from actual practice. Yocum in America and Sody in Lüttich found that in mixtures with many extracts the available tans were low-

ered. Various results have been obtained with quebracho. It appears that cellulose extract does enable more of the difficult soluble tans of quebracho to remain in solution.

The principal use of cellulose extract so far has been in loading. It ought to be cheap and penetrates well, although if a certain limit be exceeded the leather becomes brittle, especially if sulphited extracts are used in tanning. The bleaching of leather loaded with cellulose is difficult because of its easy solubility and the proneness to spotting. Brittleness can be reduced by adding acid oleates (sulphonated elain). Large amounts of fat are needed, however, which darken the leather and bleaching with soda and acid is needful.

It is more difficult to point out the utility of cellulose extract as an agent in tanning. The directions for its use are not specific and always require the presence of other tanning materials. In one way it may assist tannage, namely by increasing the diffusibility of certain tans such as those of unclarified quebracho and some brands of oakwood. It is best added to their hot solutions, 20 per cent. sufficing to raise the quality, although more is needed if greater speed is required. It can thus be utilized to hasten a foretannage, here in combination with a good grade quebracho. To profitably secure these useful results, it will be necessary that the present price of cellulose extract be lowered. W. J. K.

Distillates from Wool Fat. J. MARCUSSON and A. v. SKOPNIK. *Zeit. angew. Chem.,* 1912 [25], 2577-80. Crude wool fat, a by-product from wool washing, is worked up either for neutral fat used as a lubricant and in making lanolin or for distilled acids used in soap making, etc. The final distillation is carried out with superheated steam at 300°-350°, yielding liquid (wool fat olein), semi-solid and solid distillates.

Wool Fat Olein.—This is pressed out like the olein from the acids distilled for candle manufacture. It contains 40-60 per cent. of liquid fat acids, the rest being unsaponifiable like mineral oil, sometimes causing errors in the interpretation of analyses. This unsaponifiable component is an oil of sp. gr. 0.900 to 0.917, consisting mainly of unsaturated hydrocarbons, with iodine no. 51-79. Unlike mineral oils they dissolve in 2 vols. hot acetic aanhydrid but separate on cooling. The hydrocarbons distil without decomposition in vacuo, and are dextro-rotary, the rotation increasing with the boiling point. Like rosin oils, they have marked drying power. The saponifiable ingredients are easly freed from unsaponifiable by extracting their potash soaps with petroleum ether according to Spitz and Hönig. From a French olein the free acids finally separated formed a red-brown liquid, sp. gr. 0.913, iodine no. 52.7, sapon. no. 208.5 (mol. wt. 269.1). Besides oleic acid (iodine no. 90, mol. wt. 282) it would seem that liquid fatty acids were present. Mineral oil may be suspected in the unsaponifiable of a wool olein if the rotation is much below +18°, or the iodine number below 51. A simple preliminary test consists in shaking 5 cc. of the original olein with 5 cc. of a mixture ethyl and methyl alcohols (9:1) at 20°; 10 per cent. mineral oil will

produce turbidity with final separation of oily drops. Rosin oil additions are likewise detected, the reaction being less sensitive, but showing 20 per cent. Rosin oil has a refractive index 1.535-1.55 while that of normal olein is 1.49-1.51 like mineral oil. To apply the Morawski color test for rosin, the unsaponifiable (which gives the same reaction) must first be removed according to Spitz and Hönig and the free acids from the soap tested for rosin.

Semi-solid Distillate (Graisse blanche de suint, soap fat).—This is crystallized out and drained from the fraction 300-310°; m. p. below 45°, contains 16-33 per cent. unsaponifiable which resembles that from olein, iodine no. 60-74. Fatty acids: solid (approx. ⅔), m. p. 45°, iodine no. 13, mol. wt. 260; liquid (approx. ⅓), iodine no. 43.8, mol. wt. 270-302.

Solid Distillate (Graisse jaune de suint, wool fat stearin).—This results on subjecting the chilled distillate above 300° to hydraulic pressure. The unsaponifiable (40 per cent.) has iodine no. 47. The fatty acids (60 per cent.), iodine no. 10, mol. wt. 320-380. Wool fat stearin is entirely unsuited for candle stock. It is used for greasing leather and belting, for impregnating water-proof paper, greasing cartridge shells, etc. It differs from real stearin in absence of crystalline structure and giving Liebermann's color reaction as well as Hager-Salkowski's for cholesterol.

W. J. K.

Reports from Practice. LUDWIG JABLONSKI. *Ledertechn. Rundschau,* **1912,** 401-2. These instances illustrate the need of properly locating complaints unjustly made against the tanner.

A highly greased belting split apart on tension into two skins. The tanner had furnished good leather and it was found that this had not been dried internally before burning in the grease. Dry leather will withstand hot fat but yields to steam.

A brittle sole leather was found to contain only 7 per cent. water, and took up 5 more on standing. In order to shorten weight, the buyer had dried the leather by heat and made it brittle.

Reclamation for a ruptured belt were shifted by the maker onto the tanner who vouched for good leather and produced some of the original stock. Chemical analysis of carefully located parallel samples proved the identity:

	Belting	Croupon
Ash	0.2	0.1
Water	13.0	12.8
Hide	32.2	32.1
Soluble	4.9	4.6
Fat:	24.2	23.2
acid number	0	0
sapon. number	138	135
iodine number	227	237
unsaponified	82	80.5
Tearing resistance	—	345 k.

Inspection showed that the lacing had been stretched, the glue joints broken, and other indications of strain; the belt had evidently been overloaded.

A supply of calfskin produced shoes that showed continuous spew on storage. This was not due to the leather but the lining drill which had been impregnated with salts. Similarly a complaint against glove leather which became discolored, hard and brittle on storage, was, after vain research in the tannery, properly laid to the dusting powder which had been adulterated with salts. W. J. K.

Perfect Utilization of Spent Tan. ANON. *Conceria,* 20, 369. Analyses of spent tan from 6 different tanneries are compared in order to determine the degree of utilization by lixiviation and extraction. The final losses in the residue varied from 2.7 to 58.0 per cent. of the tanning substances originally present. A mixture of pine and oak bark and nutgalls was used in the tannery which showed the smallest loss.

H. S. PAINE.

Use of Aluminum Sulphate in Tanning. ANON. *Conceria,* 20, 343-4. In the process described the skins are first immersed in a bath which consists of 1 part aluminum sulphate and 12 parts water. The organic compounds of the green skins cause the reduction of some of the aluminum sulphate with liberation of sulphur dioxide; the latter causes swelling of the skins and also has a bleaching action. Addition of hydrochloric acid to the bath accelerates the liberation of sulphur dioxide and thus facilitates the action; aluminum chloride thus formed, as well as the aluminum sulphate, penetrates and impregnates the skin, this action being favored by the swelling produced by the sulphur dioxide. This bath is continued for 10-40 minutes, according to the quality of the skins; the latter are then removed and, after being allowed to drain, are placed in a bath consisting of 12 parts by volume of water and 1 part of concentrated ammonia water. The latter neutralizes the free acid present, while the precipitated aluminum hydroxide has a tanning action and serves as a mordant in case the leather is dyed. These operations are completed by placing the skins in revolving casks with a thick paste consisting of 8 parts flour and 1 part glycerine to which a small quantity of the precipitate from the ammonia bath has been added. The skins are not removed until this paste has been completely absorbed; they are then finished in the usual way.

H. S. PAINE.

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CORRECTIONS.

In the April number, in Table 2 of the article on Analysis of the Tannins by L. E. Levi and A. C. Orthmann, page 162, third line from bottom of page, 21.89 should be 21.98, and on page 163, last line of the table, 17.48 should be 27.48.

A BACTERIAL STUDY OF THE BATING PROCESS.

By Wm. Cruess and Frank H. Wilson.

California tanners, who have tried both dung and acid bates, find, in the production of light and, to a less degree, heavy leathers, that the manure bate produces a superior article. The chief objections to the manure bates are their disagreeable appearance and odor and the danger of overbating or of producing discolored hides. In spite of these objections, they are still used in most cases where light leathers are made.

The following study was undertaken in order to determine the character of a few of the bacteria occuring in pigeon manure bate, with the purpose of utilizing a pure culture of bacteria in place of the present somewhat objectionable method. Such a substitute has been worked out in Europe by Becker and Wood[1] in "Bacillus Erodiens," grown on a substance called Erodin. It is claimed that this preparation gives uniform results without danger of overbating or discoloration. Oropon[2] is in use in several California tanneries. A recent English[3] patent bate makes use of pure cultures of bacteria from dog dung.

In the tests at the University of California[4] pure cultures of bacteria were made from pigeon manure bate, from liquor in use in the bating tank and from old bating liquor. The method of purification was repeated by plating on agar bouillon. It was found that several platings were necessary to insure pure cultures, since the bacteria tend to form zooglaeal masses in which several varieties may be present, but produce only one colony on the agar.

The following descriptions aim to give an idea of the properties of the organisms studied. For convenience, they will be referred to by their laboratory numbers. The methods used in the study of the morphological and biochemical properties of the bacteria are those given in Jordan's General Bacteriology and Chester's Manual of Determinative Bacteriology. The data thus obtained are summarized in Tables I, II, and III.

[1] J. T. Wood, *Jour. Soc. Chem. Ind.*, 19 o, 666.

[2] Dr. Rohm, Am. Patent, 895,382. Dec. 1, 1907.

[3] *Jour. Soc. Chem. Ind.*, 1911, 1078, Eng. patent, 24,982, Oct. 27, 1910.

[4] The samples of bate etc., were furnished by the Norton Tanning Co. of San Francisco. They also allowed us to carry out several tests in their tannery.

TABLE I.—MORPHOLOGICAL PROPERTIES OF BACTERIA FROM BATING LIQUOR.

No. of organism	Average size	Shape	Spore formation	Motility	Number	Flagella	Gram's stain	Chain formation
1	1.2μ x 0.6μ	Short, diplo-bacteria	Positive 1 to 3 spores per cell	Non-motile	1	No flagella	Positive	In pairs
2	1.2μ x 0.9μ	Short, thick rods	Negative	Rapidly motile	2	2 to 10 peritrichic flagella	Positive	Single cells
3	1.2μ x 0.6μ	Short rods	Negative	Rapidly motile	3	2 to 10 peritrichic flagella	Negative	Single cells
4	0.9μ x 0.6μ	Short thick rods	Negative	Less motile than 2 or 3	4	Peritrichic, cells of uneven length	Positive	Single cells
5	1.0μ x 0.6μ	Short rods	Negative	Non-motile	5	No flagella	Positive	Long chains
6	7.2μ x 0.6μ	Long rods	Negative	Non-motile	6	No flagella	Positive	Single cells
7	2.5μ x 0.6μ	Medium rods	Negative	Sluggishly motile	7	2 to 6 peritrichic flagella	Positive	Single cells
8	6.0μ x 0.6μ	Long rods	Negative	Non-motile	8	No flagella	Positive	Single cells
9	1.2μ x 0.4μ	Slender rods	Negative	Sluggishly motile	9	1 to 2 flagella at each end	Positive	Single and in chains of 3 or 4
10	1.2μ x 0.6μ	Short rods	Negative	Sluggishly motile	10	6 to 8 peritrichic flagella	Positive	Single cells

TABLE II.—GROWTH OF BATE BACTERIA ON SOLID MEDIA.

Laboratory Number	Agar Colonies	Agar Slant	Gelatin Stab
Bact. No. 1	Large; yellowish; white; contoured surface; flat; edges auriculate; odorless. Finely granular under 1 in. objective.	Heavily beaded growth along line of slant.	Beaded growth along line of puncture. No liquefaction.
Bact. No. 2	Medium sized; white; smooth surface; edges undulate; faecal odor. Coarsely granular under 1 in. objective.	Broad, flat growth with deep indentations giving appearance of separate colonies.	Beaded growth along line of puncture.
Bact. No. 3	Medium sized; translucent and resinous; color brown; surface flat and smooth; edges undulate; odorless. Finely granular under 1 in. objective.	Broad, flat, corrugated growth.	No liquefaction.
Bact. No. 4	Spreading rhizoid colonies; color, yellow; surface, flat and smooth; under 1 inch objective, edges lacerate with fine streamers.	Spreading irregular growth.	After 5 days very slight liquefaction at surface; after 3 weeks almost completely liquefied.
Bact. No. 5	Medium sized round flat colonies; surface smooth; edges smooth; odorless.	Smooth white growth.	Saw tooth like growth along line of puncture; no liquefaction.

TABLE II.—GROWTH OF BATE BACTERIA ON SOLID MEDIA.—*Continued.*

Bact. No. 6	Large; contoured surface; color brownish; luster resinous; edges undulate. Coarsely granular under 1 in. objective.	Effused resinous growth tending to cover whole surface of slant.	Beaded growth along line of puncture, no liquefaction.
Bact. No. 7....	Large; flat; white; cretaceous; edges lacerate; center depressed; odorless. Under 1 in. objective edges auriculate.	Heavily corrugated growth along line of stroke; chalky appearance.	Rapid liquefaction from surface downward. Whole tube liquefied in three weeks.
Bact. No. 8	Very large rhizoidal colonies; flat; yellow; surface smooth; faint hide odor. Under 1-inch objective finely granular.	Arborescent or branch like growth.	Vigorous surface growth and growth one-half in. below surface along line of puncture; no liquefaction.
Bact. No. 9	Medium sized round colonies; flat; white; semi-translucent; edges smooth. Under 1-in. objective coarsely granular.	Broad flat growth, not beaded or corrugated.	Vigorous surface growth; slight growth along line of puncture; no liquefaction.
Bact. No. 10...	Large; flat; yellowish white; edges smooth; colonies in agar, biconvex; slight hide odor. Under 1-in. objective finely granular.	Broad flat surface with edges undulate.	Beaded growth along line of puncture; bubbles of gas in the gelatin.

TABLE II.—*Continued*

Laboratory Number.	On Potato Blocks.	On Nutrient Starch Jelly.
Bact. No. 1	Heavy, grayish white growth	Heavy pink growth at surface; no liquefaction.
Bact. No. 2	Scanty, smooth, light brown growth.	Scanty, colorless surface growth. No. liquefaction.
Bact. No. 3	No growth.	Colorless surface growth; no liquefaction.
Bact. No. 4	Heavy grayish white growth.	Vigorous surface growth; color, white; no liquefaction.
Bact. No. 5	No growth.	Transparent, slimy surface growth ; no liquefaction.
Bact. No. 6	Very slight, watery growth.	Slight, colorless surface growth; no liquefaction.
Bact. No. 7	Very heavy, wrinkled, honeycombed growth; slimy at the bottom of the tube.	Heavy. cretaceous growth ; no liquefaction.
Bact. No. 8	Very slight colorless growth.	Transparent surface growth; slimy. No liquefaction.
Bact. No. 9	No growth.	Light, yellow growth ; no liquefaction.
Bact. No. 10 ...	Smooth, yellow, slimy growth.	Transparent, slimy growth; no liquefaction.

In Table No. III the column giving the acid formation in dextrose, such figures as + 3.3,—.7 etc., will be found. These refer to the increase if + and to decrease if — of cc. of normal sodium hydrate necessary to neutralize 100 cc. of liquid as compared to the number of cc. so used on the liquid before bacterial growth took place.

TABLE III.—BIOCHEMICAL PROPERTIES OF BATE BACTERIA.

Number	Ammonia formation	Indol formation	Ratio $H:CO_2$ lactose bouillon	Ratio $H:CO_2$ dextrose bouillon	Acid formation in dextrose bouillon	Growth in litmus milk	Growth in plain milk
1	Slightly positive	Fairly strong	No gas	No gas	+0.8	Slow reduction of color. Final decoloration	Vigorous growth, no coagulation or dissolving of casein
2	Slightly positive	Negative	3:2	9:1	+4.1	No action on color. Dissolves casein	Slowly forms a soft curd
3	Slightly positive	Strongly positive	No gas	No gas	+2.7	Reduces the color of litmus	Slowly forms a soft curd; no resolution
4	Slightly positive	Strongly positive	No gas	No gas	0.0	Litmus turns slightly acid in color	Good growth, no action on casein
5	Slightly positive	Negative	No gas	No gas	—0.6	At first acid, later decolorizes the litmus	Casein dissolved without previous coagulation
6	Strongly positive	Negative	No gas	No gas	+0.9	Litmus remains neutral	Forms jelly like curd, with separation of curd and whey

TABLE III.—BIOCHEMICAL PROPERTIES OF BATE BACTERIA.—*Continued.*

Number	Ammonia formation	Indol formation	Ratio $H:CO_2$ lactose bouillon	Ratio $H:CO_2$ dextrose bouillon	Acid formation in dextrose bouillon	Growth in litmus milk	Growth in plain milk
7..........	Strongly positive	Strongly positive	No gas	No gas	+3.3	Decolorizes litmus slowly	Gives a slimy curd, that redissolves to give a clear solution
8..........	Strongly positive	Negative	No gas	No gas	0.0	Not completely decolorized in two weeks	Very slow and incomplete liquefacton of the casein, with formation of curd
9..........	Strongly positive	Negative	No gas	No gas	—0.7	Gives an alkaline reaction after two weeks	Growth same as No. 8
10..........	Strongly positive	Negative	7:3	4:1	+4.6	Strong acid, reaction to litmus in 24 hours	Curdles the milk rapidly without redissolving the soft acid curd formed

The observations given in Table No. I were made on young bouillon cultures of the organisms. An examination of the results summarized in Tables I, II and III give a fair idea of the morphology and culture characteristics of the bacteria. Without much doubt culture No. 7 is bacillus subtilis or a closely related form. Culture No. 2 is a variety of Bacillus Coli, since it complies with the cultural characteristics and morphology of B. Coli. No. 10 is similar in many respects to No. 2; it differs from it in that it has no odor, whereas, No. 2 has a decided faecal odor. No. 10 gives more rapid formation of acid than No. 2; No. 2 forms acid from dextrose but not from milk sugar, whereas No. 10 forms acid from both of these sugars. Both No. 10 and No. 2 form gas in lactose and dextrose bouillon.

An interesting thing to note is that only one of the cultures under observation gave rapid liquefaction of the gelatin. This would indicate that the bating liquor, from which these bacteria were taken, has a small content of aerobic proteolytic bacteria; that is, the predominating types do not have the power to remove hide substance. Their principal action would be the removal of lime.

Figure No. 1 gives the appearance of several different kinds of bate bacteria stained to show the flagella.

The organism No. 9 is crescent shaped with flagella at both ends, whereas the other bacteria that showed flagella were straight rods and exhibited flagella on all sides.

LABORATORY TESTS OF BACTERIA ON LIMED HIDES.

The following laboratory tests were undertaken to see which bacteria would appear most promising for tannery experiments. In the first experiment ordinary pigeon dung was boiled and filtered and the filtered liquid made to about 1 per cent. total solids by dilution with water. This was distributed among several flasks, sterilized and inoculated with the cultures described above. After 24 hours growth at 37 degrees C. a small piece of limed hide was put in each flask. The pieces of hide bated quickly but on continued standing were attacked and severely rotted, presumably by the bacteria in the hide, as the hide was not sterilized before the experiment. The boiled pigeon

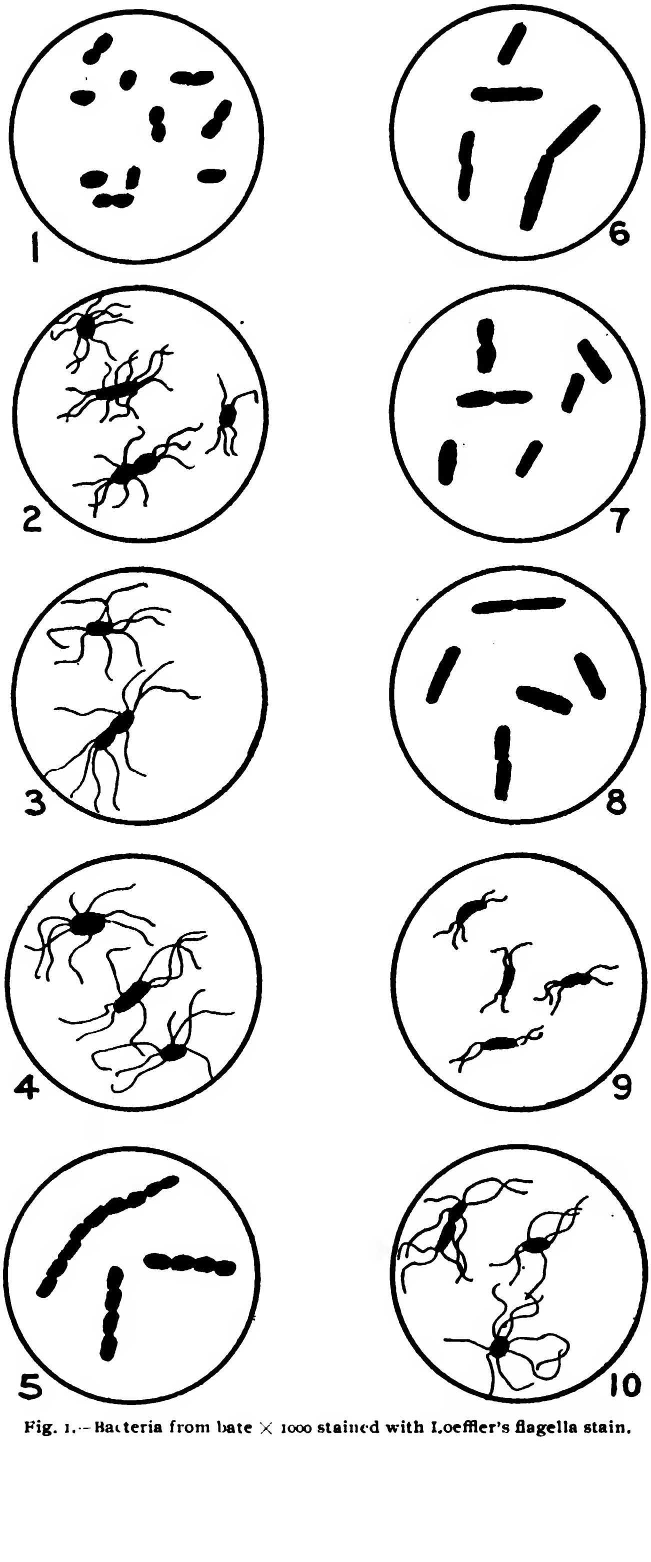

Fig. 1.—Bacteria from bate × 1000 stained with Loeffler's flagella stain.

manure is also objectionable as a bating liquid because it darkens the hide placed in it and consequently it would probably be of little use on a commercial scale.

Another test was carried out using a series of four different solutions namely, beer wort diluted to 1 per cent. Balling,* molasses in dilute solution, milk diluted to 1 per cent. Balling and the boiled and filtered pigeon manure of 1 per cent. solids. The milk proved the best of those tried out in this test, since the bacteria grew with greater rapidity in it and the decomposing action so noticeable in the natural bate was entirely lacking, while the softening effect desired in bating was all that could be desired. The growth in the wort was less vigorous than in the milk or pigeon dung but the absence of any over bating effect on long standing was noticeable. Growth in the molasses was very slight, due perhaps to excess Ca salts used in defecating the original beet juice or to an insufficiency of nitrogenous and inorganic salt bacterial food material.

A comparison of the depleting action of the natural bate and that of pure cultures of bate bacteria in wort is brought out by the following figures. The data given was obtained by growing the pure cultures of the bacteria listed below in the 1 per cent. beer wort and as a control, a mixed culture of the naturally occuring organisms of the pigeon manure in filtered 1 per cent. pigeon dung infusion. Into 24 hour cultures of these bacterial growths were placed small pieces of hide of the same weight. These pieces were cut from the same hide. The solid contents of several pieces of the hide was determined before bating by drying to constant weight in the drying oven, first at 40 degrees and finally at 100 degrees C. The pieces of hide used in the tests were assumed to contain the same amount of solid material as that of the samples used for analysis, since the piece of hide from which all the samples were cut was of uniform thickness and appearance.

After 12 and 18 hours respectively samples of the hide from the wort and dung bates were removed and a moisture determination made as described above. An examination of the results

* For sugar solutions the Balling hydrometer indicates directly the percentage of sugar contained.

will show the strong depleting action of the pigeon dung bate as compared to that of the pure cultures in the beer wort.

TABLE IV.—COMPARISON OF DEPLETING ACTION OF NATURAL PIGEON DUNG BATE AND PURE CULTURES OF BATING LIQUOR BACTERIA IN ONE PER CENT. BEER WORT.

Culture	Per cent. loss of hide substance after 12 hours bating	Per cent. loss after 18 hours bating
Mixed culture ordinary pigeon manure bacteria	12.57	25.66
Culture of bacteria No. 2 in 1 per cent. wort	—	1.33
Culture of bacteria No. 4 in 1 per cent. wort	5.6	10.8
Bacteria No. 7 in 1 per cent. beer wort ..	—	3.3
Bacteria No. 8 in 1 per cent. beer wort ..	4.4	8.4

Since the chief difference in the two solutions used above is in their sugar content it was thought to be useful to see if the addition of sugar to the ordinary bate would have any effect on the overbating action that is so characteristic of this material. Accordingly the ordinary dung bate made up in the proportions used in the tannery was divided among four large flasks. To the first flask was added no sugar; to the second, 0.5 per cent. cane sugar; to the third, 1 per cent. cane sugar, and to the fourth, 0.5 per cent. dextrose. The hide in the bate without the addition of any sugar bated rapidly and was in proper condition in 24 hours at 37 degrees C, but from that time on rapidly decomposed and in two weeks was almost completely dissolved. The hides in the 0.5 per cent. cane sugar and 0.5 per cent. dextrose plus ordinary pigeon dung infusion bated more slowly than the sample described above, but reached a soft and silky condition in four days. After three weeks at 37 degrees the samples were still in a soft and pliable condition and the grain was in no way attacked. The hide in the 1 per cent. cane sugar plus ordinary dung infusion after a few days became plumped and hard, due to the formation of acid. The grain was not attacked in this sample even after three weeks in the bating liquor. The lessons to be gained from these tests are that under the condition of the tests 0.5 per cent. cane sugar protects against over bating, while at the same time allow-

ing a soft and pliable bated hide to be obtained. This would lead us to suppose that a pack of skins could be placed in the bating liquor to which 0.5 per cent. commercial glucose had been added and could be left without further attention and without fear of overbating. The protective action of the sugar is perhaps due to the formation of acids which would inhibit the growth of putrefactive bacteria that destroy hide substance. The fact that the 1 per cent. cane sugar plus ordinary dung infusion caused a plumping of the hide might lead us to suppose that such a mixture might be of service in pulmping very heavy hides where as little depleting action as possible is wanted and removal of the lime is desired. A cheap source of sugar such as molasses or commercial glucose could no doubt be used.

In the table given below will be found data on the comparative bating effect of the various pure cultures of bacteria under observation. Fresh skimmed milk was diluted to approximately 1 per cent. Balling and divided among a series of wide mouthed flasks plugged with cotton wool. The milk was sterilized by intermittent sterilization before being inoculated with the pure cultures to be used. Each flask was inoculated with the same size starter and allowed to incubate for the same length of time before adding a piece of limed hide sterilized in 50 per cent. alcohol to each. A check flask containing ordinary pigeon manure was started at the same time. The column labeled "reaction" gives the reaction of the cut surface of the hide to litmus or phenolphthalein. This test is used as an indication of the removal or neutralization of the lime; e. g. when the hide reacts alkaline lime is assumed to still be present while if no alkaline test is given it is taken for granted that all the lime is neutralized or removed. The exception to this rule is where vigorous putrefaction has set in. In this case amines and ammonia liberated in the putrefaction process will give an alkaline reaction to litmus etc., when all the lime has been replaced by ammonia. This phenomenon is brought out in the test on the natural bate in the following table. At the beginning of the experiment with natural bate the hide reacted alkaline due to excess lime; next it reacted neutral in-

TABLE V.—COMPARISON OF PURE CULTURES OF BATE BACTERIA IN MILK WITH NATURAL BATE AS A CONTROL.

Culture	After 16 hours		After 21 hours		After 44 hours		After 65 hours	
	Reaction	Condition of hide	Reaction	Condition of hide	Reaction	Condition of hide	Reaction	Condition of hide
Ordinary bate	Slightly alkaline	Stiff	Neutral	Soft and pliable	Alkaline	Pliable and silky	Alkaline	Badly decomposed. Rapid gas evolution
Bact. No. 2	Slightly alkaline	Stiff	Neutral	Partially bated	Acid	Rough, milk curdled	Acid	Well plumped and rough
Bact. No. 3	Slightly alkaline	Stiff	Neutral	Stiff	Acid	Soft and silky	Acid	Soft and silky
Bact. No. 4	Slightly alkaline	Stiff	Neutral	Stiff	Acid	Soft and silky	Acid	Soft and silky
Bact. No. 5	Alkaline	Stiff	Faintly alkaline	Stiff	Acid	Soft and silky	Acid	Soft, but beginning to plump
Bact. No. 7	Neutral	Partially bated	Neutral	Well bated; soft and silky	Acid	Soft and silky	Acid	In excellent condition
Bact. No. 8	Slightly alkaline	Stiff	Neutral	Stiff	Acid	Stiff	Acid	Stiff and well plumped
Bact. No. 10	Neutral	Stiff	Neutral	Stiff	Acid	Partially bated	Acid	Well plumped and stiff

Fig. 2.—Comparison of action of natural bate and pure culture of bate bacteria in dilute milk.

No. 1. Bated 14 days in pigeon dung bate. No. 2. Limed hide before bating. No. 3. Hide bated 14 days in pure culture of bacteria No. 3.

dicating removal of the lime, and finally when violent putrefaction had set in the cut surface of the hide reacted strongly alkaline.

This test brought out the fact that some of the bacteria have the power to soften the hide whereas others gave a plumping action. This latter property is due no doubt to the formation of considerable quantities of lactic acid formed from the lactose of the milk. The destructive action of prolonged bating in the natural bate is again brought out by this series of tests, since after 65 hours the hide in this liquor was very badly attacked by the bacteria. A piece of the hide was left in culture No. 3 and in the natural bate for fourteen days. The condition of the hides at the end of this time is indicated by figure No. 2. The hide in the pure culture was still in excellent condition with the grain intact, whereas that in the manure bate was discolored and full of holes due to the decomposing action by proteolytic bacteria.

TANNERY TESTS.

As a result of the above tests it was decided to use dilute skimmed milk and pure cultures of bacteria Nos. 3, 7, and 8, in comparison with the pigeon manure bate at the tannery of the Norton Tanning Co., San Francisco. The cultures were grown on undiluted milk at the laboratory and were then taken to the tannery and diluted to about 1 per cent. Balling. The liquids were placed in 2 gallon wooden buckets and a piece of limed calf skin about one foot square was placed in each. For comparison a piece of the same hide was bated in the bating wheel in pigeon manure bate in the manner usually employed at the tannery. The hide in the pure cultures was bated twenty-six hours and then put in the tan pits with the other hides bated on that day. When they were removed from the bate, No. 7 was in excellent condition, *i. e.*, it had bated sufficiently and exhibited the soft and silky condition of a well bated hide. No. 3 and No. 8 however were still alkaline and the hides had not appreciably fallen. The cut surface of No. 7 was neutral to phenolphthalein, indicating sufficient bating. No. 7 came out of the tanning liquor in excellent condition making as good a leather as the piece that went through the regular bating process. A piece of hide left in No. 7 for three weeks showed no signs of overbating while a

similar piece left in the natural bate rotted almost completely away in the same time. Another sample of the natural bate to which was added a little cane sugar and left three weeks showed no evidence of decomposition, thus demonstrating the protective action of sugar against overbating.

SUMMARY AND CONCLUSIONS.

Ten different varieties of bacteria were isolated from fresh bating liquor of a San Francisco tannery and their general properties studied. It was found that several of these gave good results when substituted for the ordinary bating liquor in laboratory tests. One of the cultures gave satisfaction when tried on a small scale at the tannery in dilute skim milk, a cheap material when used in the dilution employed in the tannery tests. The bacteria were used only in the liquid cultures; for commercial purposes a solid culture would have to be developed that could be used as some of the patent bates are at present. Work is being done in the laboratory at the present time on this side of the question by H. W. Noble. Small amounts of sugar added to the natural bate seem to protect the hide against overbating. For this purpose a cheap form of sugar such as glucose or molasses could probably be used without greatly increasing the cost of bating. In fact it would probably add very little to the cost because the laboratory tests indicated that such a bate could be used for a much longer time than the ordinary bating liquor, because the growth of decomposition bacteria is considerably inhibited by acids. Furthermore, the acids formed in such a bate would hold more lime in solution per unit volume than would ordinary pigeon manure which is low in substances that yield acid.

FROM THE ZYMOLOGY LABORATORY OF THE UNIVERSITY OF CALIFORNIA EXPERIMENT STATION, BERKELEY, CAL.

PROBLEMS FOR THE LEATHER CHEMIST.

(A Lecture to the Students of Iudustrial Chemistry at the University of Michigan, Ann Arbor, Mich., by Philip M. C. Armstrong on March 5, 1913.)

HISTORICAL.

Next to the making of weapons the process of tanning is probably the oldest industry known to man. Long before cloth was invented, primitive man covered himself with the skins of the animals he had killed for food and soon discovered that these skins could be made less putrefiable by rubbing them with grease. The American Indians prepared leather in this way, and even now the Eskimo women make a very soft and pliable leather by chewing the oily skins of seals, so as to drive the grease into the skin. The greases are gradually changed to complex aldehydes, which produce a tannage somewhat similar to the modern aldehyde tannages. It was noticed that the barks of trees had the property of rendering the skins imputrescible also, and this was the beginning of the many processes of making leather by means of tannin—bearing vegetable substances which are in use to-day. We know that the art must be very ancient, as we find vegetable tanned leather in Egyptian mummy cases and in Roman remains. One of the disciples of Christ lodged at the house of a tanner in Joppa. Through the centuries the processes have of course changed a great deal, but in the main the changes have been in reducing the time necessary to tan by making the tanning liquors stronger, and by the introduction of new materials grown in remote parts of the world.

SCOPE OF THE CHEMIST.

The work of the chemist has been, so far as the vegetable process is concerned, principally to advance theories of tanning, which have enabled us to improve our technique, and to invent methods of analysis, which help us to keep a better check on the character of the tanning. A skilled chemist can frequently foresee conditions in the tan-yard, which might ruin the leather, and show how to correct them before it is too late. But useful as the chemist has been in this regard his true field lies beyond this point.

It is a matter of common knowledge that many of the materials used in tanning are growing scarce. Oak bark, which once was the staple tannage, is now very hard to get, and there are very few, if any, tanners who use it exclusively, although many claim to do so. Hemlock bark is still comparatively plentiful, but the past few years have seen it double in cost, and it is only too evident that we will have seen the last of it much sooner than we like to contemplate. And so with nearly all of the tannin bearing barks and woods. Sooner or later we shall find ourselves face to face with a scarcity which will make it impossible to go on in the time honored ways. Were it not for the mineral tannages which have already been introduced, we would be in that condition now. There are a few tanning materials, such as gambier, myrobalans and valonia, which are annual crops. These, of course, we will always have, but they would not be sufficient to meet the demand. In any case they are not satisfactory when used alone, and are useful chiefly in combination with barks and woods, so they cannot be considered, especially as they are already too costly for extensive use.

TANNAGE OF THE FUTURE.

It is quite clear that the tannage of the future must be done with materials which are the product of the laboratory. It is here that the chemist will have to help us out. He has already given us the chrome tanning process, and a successful chrome tannery without a chemist of some sort would be an impossibility. But he cannot rest on his laurels. He has a long way to go yet.

DEFINITION OF TANNING.

Tanning may be defined as a process of rendering the hide of an animal resistant to putrefaction. Leather is animal skin prepared in such a way that it will resist the destructive action of bacteria. This is accomplished by rendering the fibers of the skin impervious to moisture, either by coating them over with a material impervious to water, or by so altering their chemical structure so that they are themselves impervious. In most tannages both of these things occur, though there are exceptions, notably aldehyde, and other similar tannages, in which there is no coating formed, and the fibers are rendered impervious, prob-

ably by oxidation or reduction. It is possible to make a sort of leather by simply completely dehydrating the skin by means of alcohol and ether. Leather so made is of no commercial importance, but I have made use of this process in a method of preparing small pieces of skin for testing the colors of tanning extracts.* I have described this process to Prof. White, and he can show it to any of you who care to see it. It is an interesting experiment, inasmuch as it is possible to produce a tanning action on a piece of skin in as short a time as ten minutes.

I said before that the chemist will have to help us devise some method of tanning with artificial agents. These are of two classes, (1) Agents which will produce a change in the chemical structure of the fibers to make them impervious to water. This includes aldehydes, quinones, and other agents whose action is probably due to a change in the fibers by oxidation. They are open to serious objection in the way of cost, and so far have not produced satisfactory commercial leather, with the exception of formaldehyde, which is employed for some purposes, but is not extensively used.

The processes which give most promise are those by which colloids are precipitated in the interior of the hide structure, and deposit on the fibers, coating them over, and possibly combining with them chemically also. To this class belong now the well known chromium tannages, and a vast number of others including the vegetable tannin tannages themselves.

This brings up the problem of synthetic tannin. This was formerly considered very important, but has now been found impracticable primarily on account of the fact that the constitutions of the tannins have never been definitely ascertained, and secondly, because there are so many of them that we could never know which ones to synthesize, even if we knew how to do it, which we do not know, and probably never will. In any case it has been shown that tannin alone does not produce a satisfactory tannage, and it is by no means certain that we could employ synthetic tannin for tanning, even if the problem were solved.

We have better chances of success if we turn our attention to tanning by means of metallic salts. The real tannage of the

* See p. 159, April number of this JOURNAL.

future lies in the development of the present imperfect mineral tannages, and the invention of other mineral tannages which will accomplish better results, of course always taking into consideration the cost.

METALLIC TANNAGES.

Mineral tannages are due primarily to the precipitation on the surface of the fibers of insoluble bodies, (hydroxides, oxides and basic salts). Theoretically speaking, any metal which forms an insoluble basic salt or oxide, could be used for tanning, but only a few of them have the strong affinity for hide substance which is necessary to secure penetration. In general, any metal which forms a colloidal solution can be used. There are certain metals, however, which appear to be especially suitable, and it has been shown that leather of a sort can be made with almost any of them. These metals are those which form alums.

THE ALUMS.

The alums are double salts. In general they are sulphates, but selenates also form alums and are known as selenio-alums. The selenio-alums are of no commercial importance however. The regular series of alums are formed when the sulphate of a monovalent metal is mixed with the solution of a trivalent metal sulphate, and evaporated. The general formula of the group is $M_2T_2(SO_4)_4\ 24H_2O$. They crystallize in the form of regular octahedra. When a crystal of one alum is put into the saturated solution of another it will continue to grow in the new solution, and it is possible to make a sort of layer cake crystal.

The monovalent metals forming alums are potassium, ammonium, rubidium, caesium and monovalent thallium. Lithium does not appear to form alums. Ostwald states that sodium does not form alums either, but other authorities have shown that it does, though not so readily as potassium. The trivalent metals which form alums are aluminium, iron, chromium, manganese, indium, gallium, lanthanum, trivalent thallium, and possibly others . As both monovalent and trivalent thallium form alums a thallium-thallium alum is possible, but it is found that this splits in two, and has the formula $Tl_2(So_4)_2\ 6H_2O$, and crystallizes in a different series, which might lead us into thinking

that thallium was divalent, as well as monovalent and trivalent, if we did not consider that it is really a half-portion of Tl_2SO_4–$Tl_2(SO_4)_3$. The only alums we need to consider are those of aluminium, chromium, iron and manganese.

The tanning properties of aluminium have been known for many centuries, and in the form of the potassium and ammonium alums is used commercially, mainly in the tanning of furs. It is an excellent tanning agent, and will some day be used much more extensively than it is at present. It has never had the recognition which it deserves.

Chromium is also used commercially, and forms the basis of the so-called "chrome" processes, which are very widely used for the production of light leathers, but so far have not been sufficiently developed to make good heavy leather. There is a big fortune waiting for the man who can invent a way to make chrome sole leather as good as bark tanned sole.

PROPERTIES OF ALUMS AND OTHER SALTS OF THE SAME METALS.

It is not necessary that we use the alums themselves in tanning, but we may use any soluble salts of the same metals, although it is customary to use the sulphates or chlorides on account of their cheapness. The alums themselves, however, are usually used, as ordinarily they are the most convenient. The salts of alum-forming metals have certain properties in common, on which their suitability for tanning depends. They are very soluble in water, which is essential, and they are unstable in solution in a peculiar way. When a salt of an alum-forming metal is dissolved in water it hydrolyzes, forming insoluble hydroxides and insoluble basic salts. In the case of chromium this occurs on boiling or the addition of alkalies, but in the others it is immediate and spontaneous. These insoluble substances do not precipitate, but remain in colloidal solution until the particles are relieved of the electrical charges which hold them in suspension. This occurs either when they come in contact with colloidal bodies oppositely charged, such as gelatine, or when they are made alkaline beyond a certain point. A fresh solution of pure chrome alum is violet, but becomes green on heating, due to the colloidal solution of insoluble green chromic hydroxide. This will, if not

made alkaline, gradually revert to the violet state, as chromium ions are stable in the cold. Similarly a solution of ferric alum is dark red, due to a colloidal solution of ferric hydroxide, even in the cold, but on acidification turns bright yellow, which is the color of the ferric ion. Manganese alums are still less stable, and after hydrolysis pass rapidly into the manganous state unless strongly acidified, and even then the reduction is fairly rapid. They appear to be more stable in mixture with other alums, and this fact has been utilized in the only manganese tannage which has ever been tried out commercially. The project was a failure, but there is no reason why new experimental work might not develop a satisfactory tannage.

COLLOIDS ARE THE TANNERS.

In all of these alum tannages the products of the hydrolysis, that is the colloids, are the tanning agents. A neutral or acid alum liquor will penetrate the skin rapidly and color it, but does not effect a tannage. This is due to the fact that the acid product of the hydrolysis penetrates the fibers more rapidly than the colloidal constituents do, and by osmotic pressure keeps the colloids out, also effecting a swelling of the hide so that it will not tan properly. This is prevented by the addition of a large quantity of a neutral salt. Common salt is usually employed. If you are interested in the chemical reason for this behavior refer to Procter, Principles of Leather Manufacture, page 81, et seq.

Though there are always some basic salts present, even when acidified, the basicity caused by hydrolysis is not sufficient, so it is customary to add alkalies to the solutions. Care must be employed not to make them too basic, otherwise the hydroxides will precipitate. Again, if the solutions are too basic, the tannage will be unsatisfactory. It has been found in chrome tanning that a basicity giving an average compound of the formula $Cr\,OH(SO_4)$ seems to work best. (Procter).

In aluminium tanning sometimes leather is tanned without the addition of alkalies, as aluminium hydrolyzes more completely than chromium, but if salt is not used the skin swells up horribly, and a very imperfect tannage takes place, so that the leather produced is horny and of no value. So salt is invariably used.

When a fine soft leather is desired eggs and flour are mixed with the alum and salt. These have no tanning value, but help to make the leather velvety and pliable. Aluminium tannage makes a perfectly white leather, which however gradually turns yellow by oxidation.

Iron can be used without alkalis also, with the addition of salt, but works much better if made alkaline. As yet it is not used commercially, but it surely will be some day, and experimental work on iron tannages is about the most promising line I could suggest.

Manganese is so unstable that very little work has been done on it, but there is no reason why a good tannage by means of manganese should not be worked out. The chemist would have to devise a way of keeping it in the maganic state, and also find a cheap way of making the liquors directly from crude manganese peroxide. It is not used commercially at all, so far as I know, but it produces a pretty, pink colored leather, that is very pleasing, and work in this line might repay investigation.

All mineral tannages require to be neutralized when the tannage is complete. This is due to the fact that although basic salts are employed, still there is free acid present, by hydrolysis. This free acid, if not neutralized, will cause the leather to become tender, and lack strength, so that it is customary to wash the tanned leather in dilute alkalis, so as to neutralize the acid. The greatest of care must be exercised not to more than neutralize the acid, or the basic salts will all be changed into hydroxides, and make the leather hard and brittle, as well as decreasing the tannage, as the tannage depends on the gummy non-crystalline character of these basic salts to a very large extent, and the hydroxides dry out hard and brittle. On this account the caustic alkalis are seldom used, and even sodium carbonate must be used with caution. Borax is about as good an alkali to use as any. It is difficult to over neutralize with borax, even when it is used in great excess, so that it is more or less fool-proof. It makes the leather softer, however, than soda does, so that when a hard leather is desired it is necessary to use soda, the precipitated chrome helping to stiffen the leather. Investigation might yield a more satisfactory alkali.

It is characteristic of all mineral tanned leathers that when they

are once dried out they cannot be completely wet up again, as bark leather can. This is due to the fact that the fibers are covered with the gummy basic salts. These, you will remember, were not in true solution, but in colloidal solution, so that when they dry out they lose their electrical charges and will not go into solution again. When we try to wet the leather the water penetrates only between the fibers, and does not wet the fibers themselves. This makes mineral tannages much more nearly water-proof than bark tannages, but is a great objection in many cases, when it is desired to wet the leather up to stretch it over a form. To overcome this fault it is customary to impregnate the leather with oil, which makes the leather softer and more permeable to moisture. Pure oil penetrates mineral tanned leather only with difficulty, so that the usual method is to emulsify the oil by means of soap and water, which mixture is called a "fat-liquor," and this fat liquor is forced into the wet leather by drumming it in a mill. It is essential that all of the free metallic salt be washed out or precipitated before fat-liquoring, otherwise there will be a precipitate of insoluble metallic soaps on the surface of the leather, which is very difficult to remove, as metallic soaps are insoluble in any ordinary solvents. I have found that a piece of leather impregnated with melted copper soap is resistant to, if not indestructible by both strong acids and strong alkalis.

OBJECTIONS TO THE MINERAL TANNAGES.

There are many objections to mineral tannages in general. Some of these have been partially solved, but others are still waiting for some clever man to come along and down them.

First and most important, no method has yet been devised to fill mineral leather up, and plump it like bark tanned leather. This is the principal thing that keeps chrome sole in a subordinate place. If some chemist can advance a method whereby a chrome tanned leather can be plumped up and solidified, without impairing its water resisting qualities, he can just sit down and loaf for the rest of his life. There are other minor objections, but the solution of one problem would probably mean the solution of the others at the same time.

The other principal objections are these.

It is very slippery when wet. In sole leather this is a great objection, and is overcome in a crude manner by stuffing in the mill with hard greases. This stops the slipping but makes the leather rubbery, so that it does not retain its shape, but squeezes out under foot, so that it is out of the question for fine shoes. Chrome sole is usually used for sporting shoes.

The edges cannot be finished like bark tanned leather, and it always looks on the edges as though it needed a shave. If we can learn to fill it up, like bark leather, this objection will disappear at the same time, as this characteristic is due to the fact that there is no interfibrillar material.

It has a marked tendency to stretch, and apparently there is no limit to the stretching, the leather becoming narrower and thinner as it stretches. Filling up would correct this fault also.

ADVANTAGES OF MINERAL TANNAGES.

On the other hand there are many things in favor of mineral tannages. In the first place the tannage is much shorter, so that the leather is finished in a few days, or weeks at most, instead of lasting over many months. This not only saves tying up so much money, but also saves lots of money in spoiled leather, because if anything goes wrong there is not so much leather involved. Moreover, in mineral tannage we are dealing with definite materials, whose chemical nature is well understood, and can be used in specific quantities. The process can be controlled absolutely by chemical analysis, and the results predicted with certainty, while vegetable tannage, in spite of all the work that has been done, is still largely a matter of guess work, and requires long experience and fine judgment. Even then the leather is never twice the same, even though every effort be made to do the same thing every time. The materials themselves are of variable constitution and are, moreover, subject to perplexing decomposition, both chemical and bacterial.

In the second place, mineral tannages are water-resisting, which for sole leather and belting, is a great recommendation. For light leathers the objections do not carry so much weight, and the amount of chrome calf-skins and side leather on the market is eloquent testimony to the desirability of the process.

Thirdly, it is far cheaper than bark tannage.

SPECIFIC MINERAL TANNAGES—IRON.

So far as I know there is no leather made commercially by means of iron, although there is one brand of upper leather said to be tanned partly by iron. As I have never seen a piece of it, I cannot say definitely. There have been numerous patents taken out for iron tanning, but none of them have been successful commercially. Whether this has been due to fundamental defects in the processes, or to bad technique, or mismanagement, I am unable to say. The fact remains that leather can be made by means of iron salts, and I believe that there is a very fruitful field for investigation along this line. Iron tannage has two things to recommend it over chrome tannage. Iron is cheaper than chromium, and the leather has a more pleasing color. Chrome tanned leather has usually a dirty, unpleasant blue color, while iron leather has a pleasing yellowish brown color, more like a vegetable tannage. It has the disadvantage that it cannot be used in combination with vegetable materials, as the iron combines chemically with the tannins to form complex ferric tannates, which are black, and also make the leather brittle. Also it is said to make a leather thinner than chrome, and less pliable, but this has not been my experience.

There have been many ways suggested of tanning with iron. Prof. Knapp patented a tanning liquor made by oxidizing ferrous sulphate with nitric acid, quite a while ago. Manganese dioxide has been employed for the same purpose, the manganese present having no tanning value however, as it was present in the manganous state. I have been experimenting on ferrous sulphate, oxidized to ferric sulphate by means of potassium dichromate, which gives a mixture of chromic sulphate and ferric sulphate, both of which are tanning agents. This gives a brown leather which promises well. There is a sample of it among the pieces I have handed to you for inspection. I have heard that iron tannage has the objection that the ferric salts are reduced in time to the non-tanning ferrous state at the expense of the hide fiber, but I have not noticed any such action. If there is such an action, however, I think that by a little experimenting it might be turned to account, as some tannages appear to depend for their action entirely on the oxidation of the fiber, so that it becomes im-

pervious to moisture. This might be a good subject for investigation. I think myself that the only fundamental objection to the iron process is that one which is common to all the mineral tannages, namely, that they do not fill up. If some method could be found of depositing in the interfibrillar space some insoluble compound with a non-crystalline structure, the whole problem of mineral tannage of heavy leathers would be solved. It must be a good non-conductor of heat in order to be satisfactory, and must be hard enough so that the leather will take a polish on the edges. Probably it would have to be organic, as inorganic bodies, as a rule, are too brittle. Possibly some form of soluble cellulose would be the answer to the problem. That is for the chemist to investigate. You see that there is plenty of work for him to do.

MANGANESE.

There has been very little work done on manganese tannages. This is due to two things. First, the instability of manganic compounds, and second, the cost of the material. The most stable manganic compound is caesium manganic alum, but that would be quite out of the question, as caesium salts are far too costly. Manganic phosphate is stable in a solution of concentrated phosphoric acid, but that would be quite useless for tanning purposes. So manganese as a tanning agent does not seem to promise much. It is much more stable in combination with other alums, but it is doubtful if there would be any advantage to be gained from its use. Iron is a much more promising material, and I fully believe that the day will come when iron tanned leather will have to be reckoned with in the market.

OTHER SYNTHETIC TANNAGES.

Besides the tannages we have taken up there are a vast number of others which have been tried out in the laboratory.

Copper is a possible tanning agent, as it forms basic salts and colloidal solutions. If ammonia is added to cupric sulphate a precipitate of a basic copper sulphate comes down ($Cu_4(OH)_6SO_4$), which dissolves in excess of ammonia to form a complex copper ammonia compound ($Cu(NH_3)_4SO_4$). This is the compound found on evaporation to dryness, at any rate.

Smith states that there is an ion $Cu(NH_3)_4$, but I doubt this. I have found that it is possible to tan leather with this solution, and think that it is probable that it is a colloidal solution of the basic copper sulphate and the hydroxide, analogous to the basic alum solutions, though I have not had an opportunity to investigate this.

Leather has been tanned experimentally with salts of cerium, though I do not know about the quality of the leather produced, as I have not tried it myself. It is a commercial possibility, as cerium is found in large quantities in the thorium residues, left over as a by-product of the manufacture of Welsbach gas mantles. These residues are now mostly thrown away, I believe, as they are of no commercial value.

Mr. Will Plumer, of Muskegon, was at one time experimenting with a tin tannage, with the idea of producing a permanent white leather, but I do not know what success he had. I have not heard him speak of it lately, and think he has given it up.

Aldehydes are used in tanning to a certain extent, but the leather produced is expensive and not very widely used. There is a well known English patent relating to formaldehyde tannage, but I have not heard much about it lately. I believe that it is still in use, however. It produces a pure white leather, probably by reduction or oxidation.

Tanning with quinone has been proposed, but I have not heard that it has been used commercially. The leather produced is white.

The latest is tanning with bromine by oxidation, but this is hardy a commercial possibility on account of the cost. This produces white leather also, and in a marvelously short time.

In fact, the materials suggested are so many that it would take a long time merely to enumerate them. Very few give much promise of commercial value.

CONCLUSION.

You will see that there are few branches of chemistry in which there is so much room for chemical research as in leather chemistry. The problems which I have suggested to you are only a few among the many which are perplexing tanners. In

the beam house, tan-yard, and currying shop there are many things that the chemist can improve, and much has been done already. Thanks to the researches of Wood, Röhm, and others, the problem of deliming and bating is fairly well solved, but there is still much work to be done by the chemist in every department of the tannery. In choosing your specialty, you will do well to consider the leather industry. Nearly every tannery of note now employes its chemist, and many of the larger ones employ several investigators. The Tanners Association is so anxious to get chemists that it has endowed a school in Brooklyn, at Pratt Institute, to help fill the demand.

In conclusion I will enumerate the principal things which the chemist can do for us.

(1) He can devise more accurate and quicker methods of analysis of materials, so as to give a better check on the processes.

(2) He can invent new tannages and show us how to use them.

(3) He can work to improve present methods, both in technique, and by addition of new processes to improve gains.

(4) He can develop the mineral tannages so as to make more satisfactory heavy leather.

There are lots of good leather chemists, but as in everything else, there is always room for a good man at the top of the heap.

A SYNTHETIC TANNIN.*

By Edmund Stiasny, Ph. D.

It has always been the desire of chemists to replace natural products by artificial substances, and especially those which are used for technical purposes. The object of doing so is to make the industry more independent of the market for natural products in general, further to obtain economical advantages, and finally to achieve results which may modify or surpass those obtained by the use of natural products. This desire to find artificial substances for technically important materials has led to the invention of artificial dye-stuffs, perfumes, silks, synthetic indigo, rubber etc., and tends to reduce the number of indispens-

* *The Leather World*, March 20, 1913, and *Collegium*, April, 1913.

able natural products to a very few, such as coal, salt, ores, water, air, etc.

There is one group of natural products which has not yet been successfully substituted by synthetic substances, viz., the vegetable tannins. Though chrome tannage has been, and will be, an important competitor of vegetable tannages, still the largest amount of leather is made by means of vegetable tannin materials and tannin extracts, and it seems rather unlikely that one could find an artificial substitute for these substances which will be able to compete with these both in effect and in price.

In speaking of artificial or synthetic tannins, one must distinguish between substances which are identical as to chemical constitution with the original tannins (as synthetic indigo is identical with purified natural indigo), and with tannin substances which show only analogies and resemblances in their constitution and chemical behaviour without being identical with the natural products, but which are capable of converting hide into leather (such substances could be comparable with aniline dyes as substitutes for natural dye-stuffs).

The first alternative, *i. e.*, the attempt to synthesize substances exactly identical with tannins as to chemical constitution involves considerable difficulties. In the first place, our present knowledge of the chemistry of vegetable tannins is rather insufficient since the constitution of most tannins, and especially of those of great industrial importance, is still an unsolved problem. The constitution of gallotannic acid, the tannin of galls, has been solved now by E. Fischer and his pupils. Catechin, the slightly soluble substance present in gambier, has been successfully investigated by Kostanecki and others, and if ellagic acid can be called a tannin, it concludes the series of those which are chemically understood. E. Fischer has embarked upon a very promising attempt to synthesize gallotannic acid, but these experiments—though extremely interesting and valuable from the scientific point of view—can scarcely lead to results of technical importance, as the price of such products would be very much higher than the price of the natural material.

We have, therefore, to go back to the other alternative, *i. e.*, to attempt to synthesize substances of a constitution similar to,

though not identical with, the vegetable tannins, and with the property of converting hide into leather. This problem again is connected with the question of the nature of the tanning process, and we all know that this latter question is not yet solved. Some of us assume the tanning process to be a chemical combination between hide and the tanning agent, either the formation of a salt or a condensation product of a more complicated form, others again—with whom I am inclined to associate myself—emphasize the semi-colloidal character of every tanning agent, assuming that the tannin is primarily absorbed, and then undergoes secondary changes on the hide fiber, without actually combining with it. From this view the artificial tannin must be similar in physical properties, and especially in its semi-colloidal character, as well as in chemical constitution, to the natural product.

It has been the object of many years' work to find a way of producing such substances, which could be cheap enough to be of more than theoretical interest. The solution of this problem—or at least one solution of it—has been achieved by the action of formaldehyde on phenolic bodies under such conditions that only water soluble products are obtained. The action of formaldehyde on phenols, it is true, has been made the object of several investigations, and is the subject of various patents, but in most of these processes the products of the synthesis are entirely or partially insoluble in water and are used as substitutes for resins, celluloids, etc.

Other patents again describe the action of formaldehyde on phenols in neutral or alkaline solutions, whereby phenol-alcohols are produced which have no tanning properties. If, however, conditions are chosen so that only water soluble substances are formed in an acid solution, the products of synthesis are very similar to vegetable tannins, not only in their physical properties, but also in respect of some of the most characteristic chemical tests, and last, but not least, as regards the tanning capacity. Obviously substances of such origin will contain a carbon bridge combining two phenolic nuclei, and it may be pointed out that the same general structure is not at all unlikely to be due to some of

the natural catechol tans, which thereby may differ from the pyrogallol tans.

As an example how such artificial tannins can be produced, the following method of working may be quoted (see the author's Austrian patent No. 58405) :—Take a phenol, *e. g.*, crude cresylic acid; heat it with the equivalent amount of sulphuric acid for a few hours to 100-120° C.; cool down, and add slowly while cooling and stirring, 1 molecule of formaldehyde to each 2 molecules of the phenol. The product obtained in this simple way is of a pasty nature, and after neutralizing the free mineral acid with alkali forms the synthetic tannin called "Neradol," showing the following properties:—It is easily and completely soluble in water, the solution being very little colored. The semi-colloidal character of the solution can be seen in dialytic experiments, and by the non-crystallising nature of the substance. Gelatine solutions produce a precipitate, ferric salts give deep blue color, lead salts and aniline hydrochloric also give precipitates.

The most important analogy with vegetable tannins, however, lies, in the fact that "Neradol" is capable of converting hide into leather. This has been proved by a great number of experiments both on a small and commercial scale, and it seems that there are many possibilities for the application of this tanning agent, both alone and in combination with other materials. The white color of the "Neradol" tanned leather, and the brightening and bleaching effect of "Neradol" when used in combination with other tannins (vegetable or chrome) may be specially mentioned.

The problem of finding artificial organic tannins, similar to, if not identical with, natural vegetable tannins, has thus found one solution, and it is to be hoped that the introduction of the above-named product, followed by other synthetic tannins, may in the future lead to a development in the leather industries similar to that brought about in the dyeing industries by the introduction of artificial coloring matters.

HOW THE TANNERY FOREMAN MAY AID THE CHEMIST.*

By H. C. Reed.

I have been requested to say a few words to you along the lines suggested by the title. My experience tells me that although there has been marked improvement within recent years in the help that the chemist has received from the foreman, yet there is still considerable room for improvement. When one stops to consider that wrong information, wrong sampling and the carelessness that so surely accompanies slipshod methods, lead the chemist to draw incorrect conclusions so costly from the "dollars and cents" standpoint, I think you will agree with me that any effort to lessen the evil is commendable.

The experience of the chemist is often sufficient guide to enable him to discover the fact that he is working upon wrong premises, but why should he waste valuable time in an endeavor to learn this; time which could so much more profitably be spent upon the solution of the problem itself? I grant you that the occasions are numerous when it is difficult for the foreman to make such deductions as will enable him to submit the information and the samples that will assist the chemist in the unraveling of the mystery, but in such event why not resort to co-operation? Let the practical experience of one aid the theoretical knowledge of the other, the two in harmony working for the common good.

THE DRAWING OF SAMPLES.

What are some of the ways in which the foreman may aid the chemist? Take the question of the drawing of samples, for example. Can there be anything more important to the chemist than to have for analysis an absolutely reliable sample? If his sample is incorrect how can his conclusions be correct? Now it may seem almost an absurdity to lay any particular stress upon a matter so apparently simple as the taking of a representative sample, but I am firmly convinced that carelessness and want of attention to detail in sampling has occasioned more disrepute to the chemist than any other single item pertinent to the analytical work of the tannery.

* *Shoe and Leather Weekly*, March 15; *Hide and Leather*, April 5, 1913. Lecture at Pratt Institute.

It is not my purpose to go into lengthy discussion of methods of sampling, but to point out a few of the errors that are commonly made. The A. L. C. A. has adopted an official method for sampling, and you have doubtless familiarized yourselves to some extent with its rulings. The preamble to the methods confines itself to admonitions that are worthy of such thoughtful consideration as will keep them always fresh in mind. It may seem improbable but the chemist even to-day is likely to receive samples of solid extracts in cigar boxes, pasteboard boxes or even paper bags. Knowing that a sample of solid tanning extract will lose water with sufficient rapidity to vary in weight in the time taken for weighing out for analysis, it is not unreasonable to expect that when the chemist receives it in conditions stated it will in no wise represent the original sample in moisture content. The folly of such crudeness may perhaps be best illustrated by the actual money loss. Say we have a solid extract containing originally 23 per cent. water, and the sample furnished the chemist in an improper container shows by his analysis but 13 per cent. water. A simple calculation will prove that at 4 cents a pound for the extract containing 23 per cent. water the loss of water represents approximately a half cent a pound. In other words, the tanner, at the water content found by the chemist, would virtually be giving 4½ cents a pound for the extract instead of 4 cents, or a loss of $150 on a small carload lot.

Particularly in the sampling of solid tanning extracts must the loss in moisture be carefully guarded against, since this loss is extremely rapid both from the exposure of the large amount of surface necessitated in reducing the sample to a proper degree of fineness and the inherent friability of the material. Bearing the caution in mind, and adhering to the directions given, there should be no difficulty in getting a fairly representative sample. I say "fairly representative" advisedly, for experience has shown that in the sampling of solid extracts something must be left to the honesty and good judgment of the individual. This is particularly true in respect to the relative proportions of the sample taken from the outer and inner portions of the mass. Samples in bags have a crumbly outer layer of a depth greater or less, depending on the age of the sample, and caused by evaporation of

water from the exposed surface. It is patent that neither the dry outer layer nor the inner portion which has not lost water will give a truly representative sample, wherefore the method leaves it to the individual to select what he considers an average. It might be possible to calculate the shrinkage in weight of the package and multiply the analysis of the sample taken from the center of the package by a factor representing this shrinkage, and thus get a fairer analysis.

FROZEN EXTRACTS.

With liquid extracts the prevention of water loss is more readily controlled, but there are other difficulties presented in the sampling that are not met with in sampling solid extracts. The freezing of liquid extracts is one of these difficulties, and presents a problem that apparently admits of no satisfactory solution. Once frozen it is next to impossible to obtain a fair sample. Usually the tanner is forced to resort to the use of live steam to unload the extract, and since the water of condensation dilutes the extract, it is out of the question to draw a fair sample from a tank or barrel unloaded in this manner. Allowing the container to remain in a warm shed until the extract has entirely thawed, and giving it a subsequent thorough plunging, will, of course, permit of proper sampling, but actually such a method is precluded by the time required to accomplish it. So practically the only resort is to leave the taking of the sample in the winter months to the extract maker, and I have enough faith in the honesty and right intentions of my fellow men to believe that the tanner will not suffer by such a concession. During the cold season I am always suspicious of a sample of liquid extract that runs abnormally low in Twaddell strength with the correspondingly lowered items in analysis. It is of course perfectly possible to draw a sample of frozen extract that will give seemingly high results in analysis, but in such event it is hardly right to assume that the sample is not representative since the range of Twaddell strength may be from 35 to 60 degrees.

INSOLUBLES AT BOTTOM.

In sampling liquid extracts in tanks, it should be borne in mind that a greater proportion of the insolubles will naturally be

found at the bottom of the tank, and that for this reason the first run of extract from the tank will not be representative. Per contra, samples taken after the settlings of the tank have run out will not be altogether fair. Yet samples have come to me that I have every reason to believe were taken from the very bottom of the tank and some that by comparison of their analyses with the analyses of the samples of the same invoice taken at another point of shipment would lead one to believe they had undergone a clarification process during transit. The methods for sampling of liquid extracts in tank cars very fairly provide fór the difficulties mentioned.

You will find trouble even in so seemingly simple a matter as the sampling of spent tans. It would seem almost unnecessary to warn against the possibility of contaminating a spent with the dust from the fresh tan, but this has happened, and since the chance of the chemist discovering it is remote you should use due precaution. The results that are sometimes gotten in spent tan analysis are truly alarming, and often unnecessarily so from a faulty sample. Sometimes it happens that pieces of the fresh tan escape proper division in the chipping. These are known as "spills." Should a sample of spent contain an undue amount of "spills" it will show by analysis an excessive amount of tan from the fact that these large pieces are not so thoroughly extracted as the average cut.

CONTAINERS MUST BE DRY AND CLEAN.

Before introducing samples of extracts into glass containers make certain that the containers are dry and clean. Unnecessary warning, you may say, but I have received samples that were unquestionably contaminated with oil, undoubtedly from the previous contents of the bottle. Let me give you an example that once came to my knowledge, from personal acquaintance with the case, of the trouble that may result from improper sampling. Samples of liquid chestnut extract received at the laboratory were reported as badly off color from iron contamination. The tanner for whom the analysis was made forthwith complained to the extract manufacturer intimating that the tank cars in which the extract was shipped had not been properly painted, the iron of

the tank thus coming in contact with the extract and damaging it, which will happen when the interior of the tank is not properly covered. A visit to the tannery very quickly located the source of the trouble, which was not the tanks, but the receptacle in which the samples were taken. This was a coffee pot of tinned iron, the tin having worn off and exposed the iron to the action of the extract. That coffee pot would shortly have been worth its weight in gold if it hadn't been discovered, and I believe the tanner was the most surprised of all concerned. Remember that iron and tanning materials are bitter enemies and keep them apart as much as possible.

Now as to the amount of a sample to be furnished the chemist. It should not be too large, of course, for the cost of sending it might exceed that of analysis, but remember that accidents are just as likely to happen in the laboratory as elsewhere, necessitating a repetition of the entire analysis. I have received liquor samples of 7 degrees Barkometer strength in 2-ounce bottles with request for complete analysis. The methods for sampling inform us as to size of samples.

You probably all know that liquors, after the removal of the hide change in acidity; generally losing in acid, infrequently gaining for a time. This means that the sample furnished the chemist may, unless precautions are taken, not truly represent the original acidity of the liquor. Hence the necessity of introducing a preservative that will keep the acid intact. Of many tried, thymol seems the most suitable, and is therefore incorporated in the methods. The presence of an anti-ferment is especially imperative where composite samples are taken over a period of time. In such case the best plan is to introduce an amount of thymol into the first portion of liquor that goes to make the composite sample in amount sufficient for the entire composite sample, calculating the 0.03 per cent. thymol recommended on the final bulk of sample anticipated.

ACID DETERMINATION.

While on the subject of liquors let me make a few suggestions regarding the acid determination. The question is one that has caused, and is causing, no little perplexity to the leather chemist.

I am not going into any lengthy comparison as to the value of various methods of acid determination, as such a discussion is not pertinent to the character of this paper. The much-heralded method for acid estimation by electrometric measurement, of which I confess to know little, has not lived up to the merits anticipated for it, but I do not claim that something will not eventually be evolved along these lines that will be of value. What we are really after is a method that will distinguish between the acids that will plump hide and those that will not; or perhaps I should say that we seek to learn what amount of hide-plumping acids are present in a liquor.

It was thought that the electro-metric method would solve the problem on the theory that it would differentiate the acids and the salts which nullify their plumping effect, but so far the results apparently indicate this end is attained only to a limited degree. We have an official method for acid determination known as the gelatine-hematine method. It depends upon precipitation of the tannin from a solution of the liquor with gelatine and measurement of the acidity of the detannized solution by titration with standard alkali, using hematine as an indicator. It is not the ideal method, but is serviceable within its limitations. The details are given under the official methods of the A. L. C. A. for tannin analysis, and I will not discuss them further than to say that the accuracy of the determination rests largely in the skill the operator has acquired from practice. Hematine is highly sensitive to various salts, the presence of which in the liquors serves to give end points in the titration that vary in color. In a liquor where oak is largely present the end point is quite different in color than with a liquor largely composed of hemlock. The analyst may be deceived at first but practice will enable him to note the change in color which indicates the true point of neutrality. The presence of sulphite-cellulose liquors is a menance to the accuracy of the method as most of these materials contain salts of aluminum which have a tendency to produce a false end point. The value of the gelatine-hematine method lies in the comparison of the acidity of liquors from the same tannery, not in comparing acidities from different tanneries. In other words, it has, in my opinion, a decided control value but

little if any service in determining the actual plumping value. As an instance of this, I know of two tanneries that are run to all practical purposes identically, one of which shows acid averaging twice as high as the other, while the stock from the lower acid tannery is plumper and the gains are greater. But if at either tannery there should occur a change in the amount of acidity the method would note this change and sound the alarm that might indicate danger.

A WORD ABOUT THE BARKOMETER.

Now a word or so anent the barkometer. The instrument is a necessity but may become an evil if its limitations are not respected. Don't fall into the error of setting it up as an idol and worshipping it, for it may prove a false god. Bear in mind that sugar, or any substance in solution, will give a barkometer reading. You may have two tannery liquors identical in barkometer strength, one with high tan content and high purity, and the other with low tan content and low purity. Remove all the tannin from a liquor and you will find that the barkometer still gives you a reading; by concentrating the detannized liquor you can make it read whatever barkometer you will. Attempts to control the yard by the barkometer alone have often led to disastrous results. There comes a time in the maintenance of a yard when the tail liquors, even though showing strength by barkometer, are practically worthless for tanning. If these are returned to the leaches they serve to lower the purity of the fresh liquors, and if the practice is continued the liquors throughout the entire yard are gradually reduced in purity and there comes a time when the quality of the leather is no longer what it was nor what it should be. Systematic analysis control will go a long way toward preventing this, but faith in the barkometer will not. Make certain that the barkometer itself is correct, for, judging from the variations in readings between different instruments it is most difficult to standardize them accurately.

WATCH THE SPENT TANS.

In leaching, keep a close watch on your spent tans. The closer you leach not only the less tannin do you destroy in the burning of your spent tan, but the higher the acid in your liquors. At

any rate, the results of my observations indicate that close leaching makes for high acid. It is true that the more drastic the extraction the lower the purity of the liquors, and as the lower purity is due to the greater proportion of non-tans, removed from the material under extraction, it is probable that it accounts for the higher acid as well, since it is the non-tans that produce acid by fermentation. The chemist tests his spents by extraction of a portion of the sample that he has previously ground to a very fine degree. His analysis shows all the tannin present that practical leaching fails to remove. Now it does not follow that if the chemist finds 2 per cent. tannin in a spent the tanner is expected to get busy immediately and find a way to so leach his bark as to surprise the chemist with a spent that shows zero tan. The tanner couldn't do it if he would. If the bark were ground tô the same degree of fineness in the leach house as in the laboratory the leaches would "pack," and the circulation of the liquors being imperfect the leaching would be imperfect. It is imperative that the preparation of the material for leaching be not too fine, and with the coarser preparation it is impossible, even with the excess of time consumed in extraction in leach house over laboratory, to remove the tan from the interior of the chips. If the chemist's analysis of the spent shows 1½ per cent. tannin on the dry basis, I think the leach house is doing very well. See to it that the fresh tan is properly ground; not too much fine, not too much coarse. I have seen dust taken from a leach after striking that was wadded into a compact mass which, on breaking open, proved to be dry and totally unextracted within.

CHEMICAL KNOWLEDGE BIG HELP.

You who have had the opportunity of gaining an insight into the chemical feature of tannery control, and who in the future may devote your time to the practical rather than the chemical side of tanning, are in a far better position to both give and receive assistance from the chemist than the practical man of the tannery who has not enjoyed your opportunities. You are better able to appreciate the difficulties of the problems that present themselves and therefore will more fully comprehend the need of supplying the chemist with all the data at your command. The

time has passed, however, when the tannery chemist was looked upon with scorn. He has proved his worth too often; has saved the tanner too many good dollars. It is truly wonderful what a variety of problems may confront one in the process of turning a hide into leather, and the difficulties that arise may not always be due to tannery conditions but may arise from some extraneous cause such as defects in the hides themselves with which the tanner had nothing whatsoever to do.

A prolific source of tannery trouble, and one to which in my estimation far too little attention is directed, is the character of the water. Hard water may effect very serious loss in the tannery in a quiet and unassuming way. It will destroy much tannin in leaching, lower acidity, produce bad color and rough grain and many minor evils. Remember that the appearance of water has next to nothing to do with its quality and be suspicious if the soap lather is poor. And, by the way, cultivate both your suspicion and your imagination; the former will cause you to note the unusual and the latter aid you in suggesting the reason.

BE SYSTEMATIC.

Above all, endeavor to run the tannery on a systematic basis. The chemist will analyse your liquors and submit you the results in plain and concise form. He will test your leather tanned in these liquors. Knowing the quality of the leather, the gains and the various items that go to make up your liquor report, you should be able to draw pretty fair conclusions as to whether you were progressing, standing still or going backward, and the why and the wherefore.

Do not forget that you have at your disposal a rather wide range of tanning materials, differing in character and properties. Some will serve to increase the acidity of your yard, others to diminish it; some to lower and some to raise the purity. A combination of these materials will usually effect greater gains than you will get from one alone. Saturate a hide with a single tanning material, it yet has the power of absorbing further quantities of another tanning material, just as a thoroughly tanned chrome leather will absorb the tan from a vegetable tan liquor.

The manufacturers of tanning extracts in this country have

made rapid strides in recent years in bettering the quality of their products. Let us hope that in time we may do away entirely with the present expensive and unreasonable process for bleaching leather by which, in order to cater to the fad that demands leather of certain standard quality of color, we are forced to remove weight that we have been at some pains to add and to endanger the quality of the leather in other respects. The use of extracts so prepared as to improve their quality in respect to the color they will impart to leather will go a long way toward correcting the evil mentioned, and if such extracts are a trifle more costly the difference will be more than equalized by the saving of the weight lost in bleaching. The improvement in extract manufacture is a necessary corollary to the increased consumption arising from the depletion in the available supply of oak and hemlock barks. And with increased use comes better knowledge of methods of using.

In conclusion I would impress upon you the need of a cordial understanding between the foreman and the chemist. Failing in this neither can be of service to the other, and their common interests suffer. Remember always, whether chemist or foreman, that the upholding of the theory you may entertain is not the thing of paramount importance, and be ready and willing to discard your theory for the good of the interests you represent so soon as it proves untenable.

BOOK NOTICES.

Leather Chemists' Pocket-Book. Professor Henry R. Procter, assisted by Dr. Edmund Stiasny and Harold Brumwell. London, E. &. F. N. Spon; New York, Spon & Chamberlain. 215 pp., 4x6 inches in size, and index; flexible leather binding; total thickness ½ inch.

The scope and purpose of this book are stated in Professor Procter's preface, which we quote in full.

"The little book which is now presented to the public is intended not as a substitute, but as an adjunct to the Leather Industries Laboratory Book. It has been found convenient in the laboratories of our Leather Department to employ in addition to the Laboratory Book, which is the regular text-book, a series of manuscript laboratory sheets, giving the course of analysis absolutely essential to the practical student, but omitting many details and variations which are important to the pro-

fessed chemist, and which are described in the Laboratory Book. As these sheets required revision, it appeared that in a more permanent form they might have uses to a wider public and especially to the students in evening classes of technical schools. Incidentally they have for the moment the advantage over the Laboratory Book of revision up to date by the senior members of my staff, who have co-operated with me, and to whom my thanks are specially due; but unfortunately many of the most recent and important developments of leather chemistry are of too abstruse a character to be included in so elementary and abridged a text-book."

Chapter titles are as follows: I, Introductory; II, Alkalimetry; III, Water Analysis; IV, Liming, Deliming and Bating; V, The Qualitative Recognition of Vegetable Tannins; VI, Sampling and Grinding of Tanning Materials; VII, Estimation of Tannins; VIII, Materials Used in Mineral Tannages; IX, Analysis of Formaldehyde; X, Analysis of Soaps; XI, General Chemistry of Oils and Fats; XII, Glucose Detection and Estimation; XIII, Analysis of Leather; XIV, The Use of the Microscope; XV, Bacteriology and Mycology.

In chapters VI and VII, the methods both of the International and American Associations are given. The source of this book is sufficient guarantee of its excellence, and its small size is a further recommendation.

SHOE AND LEATHER TRADE IN FRANCE AND SWITZERLAND.
SHOE AND LEATHER TRADE IN SCANDINAVIA.
SHOE AND LEATHER TRADE IN RUSSIA.

The first of these three pamphlets is issued by the Bureau of Manufactures, Department of Commerce and Labor, and the other two by the Bureau of Foreign and Domestic Commerce, of the same Department. They are all by Arthur B. Butman, Commercial Agent of the Department of Commerce and Labor. They are designated as Special Agents Series, Numbers 57, 63 and 68. These publications, embracing together a little more than 100 pages, include a great deal of matter of interest to leather men. Statistics of shoe and leather manufacture, including working conditions and wages, and description of methods are a part of the contents. These pamphlets may be obtained on application to the Bureau of Foreign and Domestic Commerce.

ABSTRACTS.

The Principles of Tanning Extract Manufacture. Lecture at Pratt Institute by George A. Kerr, *Hide and Leather*, April 5, 1913. Five stages in the manufacture are given: grinding, extraction, decolorization, concentration, drying and powdering. The "hog" and the disc chipping machine are described. The latter requires forced feed, but it requires less power, and gives more uniform results. After being coarsely chipped, the wood

is passed through the shredder. The ground wood is tested by means of a set of three screens, with ⅜, ¼ and $^1/_{12}$ inch mesh respectively. Well prepared wood will all go through the ⅜ mesh. Not more than 20 per cent. should be caught by the ¼, and not more than 10 per cent. should go through the $^1/_{12}$. Three methods of open extraction are described, decoction, diffusion and percolation. In all of these, the water is run upon a leach which is nearly spent, and the liquor obtained from this is passed over another leach which has more soluble material remaining, then over another still newer, and so on, until finally it is passed over a leach filled with new wood. In the diffusion system, the liquor moves forward continuously toward the new wood. When the tail leach is exhausted it is cut out of the series, emptied, and refilled. In the decoction system, the liquor on a leach, after absorbing all the solubles possible, is drawn off before the next weaker liquor is put on. This process is more difficult to control than the former, but causes less loss of tannin, and the author prefers it to any other open method. In the percolation method, the water or liquor is fed to the leach by a rotating sprinkler, and drawn off at the bottom. The liquor is kept hot in all these methods by a steam coil in the space under the false bottom of the vat in which the liquor accumulates. Many European extract makers use pressure extraction apparatus, called autoclaves. These are made of copper, and are worked in batteries of six or eight. When they are filled with wood, the cover is bolted on, and extraction carried out at a pressure of one to two atmospheres.

The tannins of chestnut wood suffer partial decomposition by hot water. The higher the temperature and the longer the time of extraction, the greater the loss. The decomposition of a part of the tannin is accompanied by a loss in the sugar content, and an increase in the quantity of gallic acid and volatile acids present. Chestnut tannin belongs to the pyrogallol group, but it seems to be capable of separation by alcohol or ethyl acetate into at least two divisions, one of which is essentially a coloring matter, and the other a straw colored product, resembling in appearance the tannic acid of commerce. The alcohol soluble portion is more easily converted by hydrolysis into gallic acid. Wood carefully extracted in the laboratory gives an extract containing only from 30 to 50 per cent. as much sugar as is found in commercial extract. From this it would appear that the drastic leaching used in extract manufacture converts other substances into sugar.

The liquor is filtered through rough filters before passing to the evaporators, care being taken to prevent loss of heat as far as possible. The best decolorized extracts are made by the use of blood albumen, for which the dried packing house blood of commerce is used. The liquor is cooled to about 30° C. and kept agitated while a strained solution of blood is added in a series of fine sprays, the quantity added depending on the degree of decolorization desired. The temperature is then raised to 70° C. to insure complete coagulation, and the liquor allowed to stand

and settle. The precipitate is drawn off through the bottom of the tank and put through a filter press to recover all the liquor possible. Most of the chestnut extract used in Europe is blood decolorized, but little of that used in this country. The process is rather expensive, but the author believes the improvement in the quality of the extract more than offsets this disadvantage. Chemical bleaching agents are sometimes used, and such extracts are fairly satisfactory in the making of light leathers, but they have not been found satisfactory for heavy leathers.

The important things in the evaporation of the liquors into extract are rapidity and low temperature. In order to produce a 25 per cent. tannin extract from liquors obtained by open leaching, about 17 parts of water must be evaporated to make one part of extract. In the case of liquors from pressure leaches, the proportion is about 10 to 1. A plant making 10,000 gallons of such extract per day from open leach liquors must evaporate about 170,000 gallons, or 1,416,000 pounds of water daily. To do this at atmospheric pressure would require 85 tons of coal or its equivalent. By the modern method of evaporation at reduced pressures, the quantity of heat needed is much less. The multiple effect evaporator is described with considerable detail. With a single effect about 8½ pounds of water can be evaporated, under perfect conditions, per pound of coal. With two effects this quantity is increased to 16 pounds, with three effects to 22 and with four effects to 28 pounds.

Dry powdered extract is made by means of a film dryer, in which a film of liquid extract is picked up by a revolving steam heated drum. This drum is enclosed in a space from which most of the air is exhausted by a vacuum pump. The dry extract is scraped off by a fixed scraper and drops into a receiver.

Utilization of Raisin Seeds. U. S. Dept. of Agriculture, Bureau of Plant Industry, *Bulletin 276*. By FRANK RABAK. From 3,000 to 4,000 tons of raisin seeds are available annually in California. These are capable of yielding about 100,000 gallons of edible sirup, an equal quantity of edible oil, and about the same amount of tanning extract containing 25 per cent. tannin. The final residue, after extraction of the tannin, may be ground into a meal whose analysis indicates that it would make a good stock food.

Depilatories and Their Influence upon Hides. R. W. GRIFFITH. *S. & L. Rep.*, Mar. 20, 1913, p. 37. Lime is not only a depilatory, but an alkaline plumping agent, which distends the fibers and saponifies the natural greases of the hide. In approved modern practice, the time of unhairing is shortened by the addition of sodium sulphide. Efforts of chemists to control the liming process have been chiefly directed to examination of the lime liquors. Such control can never be effective unless it includes examination of the hide also. Lime possesses several advantages over other depilatories. Its limited solubility, making excess impossible, and its mild action on the hide fiber are chief. Chamois leather and aldehyde

leather depend upon the presence of lime in the skin. It is not impossible that aldehydes of the tannins, which are organic acids, are concerned in ordinary vegetable tanning, and that the presence of lime in the hide tends to make the tannage more permanent. Sodium sulphide dissolves the hair. It undergoes partial decomposition, with the formation of caustic soda, which has a vigorous plumping action. When it is mixed with lime, it decomposes into caustic soda with the formation of calcium sulphide. This combination hastens the action of the lime, but too much sulphide must not be used, or the resulting caustic soda will injure the hide. A good test for the proper quantity is that the hair when removed should not be tender. Calcium sulphide alone acts well as a depilatory, and swells the hide but little. A combination of lime and red arsenic, slaked together, forms calcium sulphide and white arsenic. The latter in inert, and almost insoluble in water. The grain of skins treated with this mixture remains fine and smooth. One objection to the use of sulphides generally is that they attack the hair without sufficiently loosening the epidermis at the roots, so that the roots and short hairs are difficult to remove. Sodium polysulphide, prepared by boiling sodium sulphide with sulphur, 10 of the former to 1 of the latter, until the solution is a deep yellow color, is a good depilatory by itself. A 3 per cent. solution, calculated on the content of sodium sulphide, is a good strength to use. The hair is removed in two or three days, with little plumping effect. Used in conjunction with lime, sodium polysulphide behaves very similarly to red arsenic.

The Bleaching of Sole Leather. ALAN A. CLAFLIN. *S. & L. Rep.*, Mar. 20, 1913, p. 39. Attention is called to the injurious effect of the soda and acid bleach on the quality of sole leather.

Drying of Skins. ANON. *Conceria*, **21**, 11. Many of the usual defects in *glacé* leather are due to lack of care in drying; the appearance of spots and the crystallization of alum may be avoided by proper methods. If possible, the skins should be dried in the open air; if this is not possible, the skins should be separated a sufficient distance from each other and a good circulation of air should be secured. Better results are obtained with dry air at 20° C. than with moist air at 30-35° C.

H. S. PAINE.

Pickled Sheep Skins. ANON. *Conceria*, **21**, 82. Pickled sheep skins may be tanned directly without removal of acid. Two solutions are prepared in the following proportions for every 100 kilos of skins: one consists of 3 kilos aluminum sulphate in 50 liters of water and the other of 3 kilos sal soda in 50 liters of water, both being dissolved by boiling. The two solutions are mixed slowly and allowed to stand until cold. The skins are first placed in a salt solution (10 kilos salt in 50 liters of water to every 100 kilos of skins) and agitated for 10 minutes; the mixed soda

and aluminum sulphate solution is then added and the agitation continued for 30 minutes. A convenient amount of chrome liquor is next added and the skins are agitated in the casks for some 3 hours until they are well impregnated with the tanning liquid. The process is completed by adding ½ kilo salt of tartar dissolved in a little water and continuing the agitation for ½ hour; it is better, however, to leave the skins over night before removing. After draining, the skins are washed for 15 minutes in a borax solution; the operation is concluded by a second washing in clear water.

H. S. PAINE.

Mangrove Bark. ANON. *Conceria*, 21, 79-80. A recent analysis of mangrove bark gives 36.50 per cent. tanning substances, 14.08 per cent. of tannin-free material, 34.38 per cent. insoluble material, and 15.06 per cent. water. The difficulty due to the reddish color produced by the bark may be partly avoided by suitable combinations and, in cases where this color is not especially objectionable, the amount of mangrove bark may be considerably increased; in any case the amount of mangrove used should be decreased in the last stages of tanning. The tannin of mangrove bark is easily extracted and is readily absorbed by hides. The content of tannin-free soluble substances is small, so that mangrove liquor does not readily become acid. Mangrove is best suited for use with acid baths. Combinations should be made with material of as different nature as possible; for sole leather a combination of 40 per cent. pine, 30 per cent. mangrove, 20 per cent. oak, and 10 per cent. mimosa gives good results.

H. S. PAINE.

New Bath Treatment for Goat Skins in Tanning. E. ANDREIS. *Conceria*, 20, 389. The goat skins are left in a bran bath for 2 hours, then placed in cold water with the addition of lactic acid, and allowed to remain all night; the next morning the skins are withdrawn and, after rinsing with pure water, are then ready for tanning. The operation may be varied by first placing the skins in the lactic acid bath and following this the next morning with the bran bath in which the skins are allowed to remain until sufficiently softened; after rinsing, the usual procedure is followed. In both cases, lime is neutralized by the lactic acid and the action of the bran consists in softening the leather. Lactic acid should be used in the proportion of 1 kg. acid to 100 kg. of the dry skins; this amount may be increased to 1.25-1.50 kg., according to the action of the bran. In addition to its purging effect, lactic acid stops any subsequent bacteriological action due to the bran, thus avoiding any difficulty from this source. It must not be forgotten that the action of lactic acid is quite distinct from that of the bran.

H. S. PAINE.

Sodium Sulphide. "L. S." in *Bourse aux Cuirs de Liege*, Mar. 9, 1913. There are two sorts of sodium sulphide in the market, crystalline and dry. The latter is more difficult to dissolve and contains more foreign

matter. The crystalline variety contains about 30 per cent. pure dry sodium sulphide, and the other from 56 to 59 per cent. The latter is proportionally cheaper. The author contrasts the unhairing action of sodium sulphide with that of lime, asserting that the former attacks only the epidermis, while the latter on account of the bacteria which flourish in the lime liquors dissolves some of the hide substance. It is claimed that on this account a higher rendement is obtained by unhairing with sulphide instead of lime. Instead of scraping hard to remove short hairs, it is well to immerse the skins in a weak solution of sodium sulphide to loosen them. For convenience in use, a quantity of the sulphide is dissolved in hot water to a solution of about 25° Bé., and the proper amount of this solution added to the unhairing bath.

L. B.

White Leather. JOSEF L. NEJEDLY. *Allgemeine Gerber-Zeitung,* Mar. 29, 1913, p. 1. The steadily rising demand for white leather has given the tanner a new problem: to make a white leather which shall surpass the old alum leather in wear and water-resistance and provide a suitable material for the white summer shoes so popular with the ladies. At every stage of the process scrupulous cleanliness must be maintained. After liming the skins are hung in warm water over night and then unhaired and worked out on the beam. A bacterial bate is best. To secure water resistance, chrome tannage must be used, preferably one-bath. An aluminum salt is used with the pickle or in the chrome bath. In the latter case the aluminum salt is rendered basic by the addition of sal soda and added to the nearly spent chrome bath in the drum. The addition of alkali precipitates a part of the aluminum as hydroxide. The milky liquid gradually clears up in the drum, and both the chrome and the alumina are absorbed by the hide as basic salts, which fact has an important influence on the desired softness of the leather. The tanned skins are horsed up for 12 hours, pressed, and after thorough neutralization, fat-liquored. The best fat-liquor is sulphonated neats-foot oil, to which are added flour and egg-yolk. The skins are again horsed up over night, and then brushed with a mixture of talc, glycerin and water and then allowed to dry slowly. They are then dampened in saw-dust and the grain buffed off. Bleaching is done with barium chloride or sugar of lead and an acid, sulphuric or oxalic, after thorough wetting in a wheel with warm water. After drying again, the leather is brushed with a dressing made of magnesia, kaolin or other white pigment and a solution of Irish moss or gum tragacanth. L. B.

Effect of Sulphited Extract on Hide. GEORG GRASSER. *Technikum,* through *Allgemeine Gerber-Zeitung,* Mar. 8, 1913, Vol. 15, No. 10, p. 11. Sulphited extracts work well in practice, and scientific examination of them has given on the whole good results. Many tanners, however, are suspicious of them. The ground of their objection is the belief that the mineral salts contained in the extract are taken up by the leather and injure its quality. To test the matter the author prepared a cold-soluble

extract by treating ordinary Argentine quebracho extract with sulphite and bisulphite of soda and treated hide-powder and hide with it. The analysis of the extract was: sp. gr. 28°-30° Bé., water 53.8 per cent., ash 1.8 per cent., soluble non-tannins 6.8 per cent., tannin 39.4 per cent. From this extract the quebracho liquor used in the experiments was prepared by dissolving 100 g. in 900 cc. of water. Of this liquor 100 cc. were shaken with 25 g. chromed hide-powder. The average of two results gave an ash of 0.086 g. in the filtered non-tan (50 cc.) and total non-tan of 0.348 g. The values calculated from the analysis of the extract are 0.090 g. and 0.345 g. respectively, showing that very little mineral matter was absorbed by the hide-powder. In a second experiment well delimed hide was used, 20 g. of hide being shaken with 100 g. of the liquor for 3 hours, and lying in it 24 hours longer. Analyses in Table I.

TABLE I.

	Before. Per cent.	After. Per cent.
Quebracho Liquor:		
Tannin	3.94	1.88
Soluble non-tans	0.68	0.71
Ash	0.18	0.164
Hide:		
Ash	0.236	0.251

Further, five pieces of hide prepared for making upper leather were treated in the same manner as the last, and five pieces of hide prepared for making sole leather. Averages of five results are given in Table II.

TABLE II.

	Upper leather		Sole leather	
	Before. Per cent.	After. Per cent.	Before. Per cent.	After. Per cent.
Liquor:				
Tannin	3.94	1.89	3.94	1.54
Soluble non-tans	0.68	0.77	0.68	0.68
Ash	0.18	0.177	0.18	0.177
Hide:				
Ash	0.115	0.134	0.205	0.215

In a further experiment, pieces of both kinds of hide were hung in the same liquor for 14 days with daily shaking, and the ash of the liquors determined at intervals. Results in Table III.

TABLE III.

Days	0	5	10	14
	Per cent.	Per cent.	Per cent.	Per cent.
Upper Leather:				
Ash (liquor)	0.180	0.182	0.183	0.183
Ash (hide)	0.138			0.131
Sole Leather:				
Ash (liquor)	0.180	0.191	0.193	0.196
Ash (hide)	0.229			0.210

The bated hide being almost free from lime gives little mineral matter to the liquor, while the other being not so thoroughly lost lime to the liquor. These results show that the absorption of mineral salts from the liquors is slight, and cannot be enough to injure the leather. In practice sulphited extract is not used alone but in mixtures, and since it tends to hold the "reds" of other materials in solution, it prevents the rapid clogging of the pores near the surface of the hide, and so serves to promote the removal of lime by the liquor. At the same time more mineral matter may be absorbed. Any injury due to this is more than offset by the more complete removal of lime, thus avoiding the danger of bad color and brittle grain due to tannates of lime. L. B.

Tannery Effluents and Their Treatment. Jos. JETTMAR. *Collegium,* **1913,** 5-9. Many processes are proposed for the treatment of this drainage, but generally without taking much account of the composition of the effluent which varies in this industry. A sole leather factory using vegetable tannage would turn out different waste from one making chrome kid. There can be no universal method suited for all cases. Analyses of tannery effluents are lacking in the literature, and the author therefore selects and re-publishes the following analyses by Dr. Spillner, the chemist of the Emscher Genossenschaft in Essen. The drainage of the Emsch water shed (tributary to the Rhine) embracing coal mines and a dense manufacturing population, offered a stupendous problem for purification undertaken by the above company. Incidentally the effluents from one sole leather factory of the district was analyzed and these results are selected from the company's pamphlet:

Effluent No.	Cc. transparency	Cc. normal		Milligrams per liter						
					Soluble			Insoluble		
		Per acid	Liter alk.	Per mang. reduced	Dried	Ignited	Cl	Mineral	Organ.	Total nitrogen
1	3.0	0.0	0.0	75.8	5351.0	4302.0	2608.0	58.5	92.5	70.0
3	12.0	0.0	0.0	32.2	143.0	104.0	44.0	—	—	56.0
4	0.0	—	68.8	12640.0	14043.0	5236.0	640.0	970.0	4345.0	1435.0
5	8.5	—	3.5	183.0	483.0	330.0	40.0	62.5	44.0	16.8
6	13.5	—	2.0	64.8	192.0	112.0	64.8	102.0	325.0	9.1
7	25.0	—	tr.	36.7	97.0	54.0	8.0	—	—	6.3
8	27.0	5.5	—	31.6	168.0	73.0	12.0	—	—	5.6
9	26.0	0.0	0.0	36.0	103.0	56.0	12.0	—	—	6.3
10	0.2	45.0	—	41080.0	22404.0	3906.0	160.0	129.0	645.0	103.6
11	12.5	41.0	—	512.0	2618.0	349.0	16.0	0.5	5.0	5.6
12	2.5	tr.	—	3792.0	1413.0	404.0	16.0	10.5	51.5	52.2

The above effluents were: 3 soaks, 14 cubic meters daily (Nos. 1, 3), the second sample being lost; after liming (sod. sulphide combination), the hides were washed in a drum, the wash water and hair let settle and

drained at night (No. 4), 6 cbm. daily; (Nos. 5, 6) two washings after striking, 16 cbm. daily; (No. 7) washing after shaving, daily 8 cbm.; (No. 8) spent liquor after deliming with dilute acetic acid, 9 cbm. daily; (No. 9) rinsing after above, 6 cbm. daily; (No. 10) spent liquor from vat fore-tannage, 10 cbm. daily; (No. 11) used swell liquor, dil. H_2SO_4, daily 16 cbm.; (No. 12) used liquor from second vat tannage, daily 16 cbm. The tannage was finished in pits, giving no effluent. The complaints against the drainage were on the score of H_2S; there was little sediment in the brook or fungus growth. W. J. K.

PATENTS.

Hide-working Machine. British Patent No. 27,766. E. WILSON, Liverpool.

Leather-staking Machine. U. S. Patent No. 1,055,717. P. C. DANIELS, Philadelphia.

Chrome Tannage by Means of Chromium Formate. British Patent No. 27,900. A. WOLFF, Cologne, Germany.

Leather Substitute. British Patent No. 27,969. R. A. MCLAURIN, Renfrewshire. Fibrous material is coated with a solution of nitro-cellulose, dried and calendered, and the process repeated several times.

Leather-treating Machine. U. S. Patent No. 1,054,329. G. V. ANDERSON, Philadelphia, assignor to Delaware Leather Machinery Co.

Leather Evening and Grading Machine. U. S. Patent No. 1,057,358. E. P. NICHOLS, Manchester, N. H., assignor to Lacene Mfg. Co., Manchester.

Artificial Leather. U. S. Patent No. 1,056,898. G. C. L. FOREL, Lyon, France. A web of textile fabric is coated on one side with varnish and on the other with a mass of loose fibers fastened on with an adhesive.

Patent Leather Dressing. British Patent No. 26,105. D. B. MACDONALD, Leicester.

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WEIGHT-GIVING PROPERTIES OF TANNING MATERIALS AS ESTIMATED IN THE LABORATORY.

By Roy H. Wisdom.

Considerable has been written, principally abroad, to the effect that the present method of tannin analysis is insufficient to determine the real tanning value of a material. The present method reports simply in terms of tannin or matters absorbed by hide powder, whereas we know, for instance, that 25 per cent. of chestnut wood tannin is not the same as 25 per cent. of oak bark tannin. Every tanner is interested in the weight-giving power of a tanning material and this article is written with the hope that at some not far distant day this determination, or at least an approximation, will be included in every official analysis of a tannin bearing material.

In order to determine whether it is possible to attain a result which compares favorably with practical experience and bring this about in the time required by the present official method of analysis, in the face of unpractical conditions necessarily imposed, an experiment was undertaken and the results are herewith submitted to the tanner to be judged as to their practical value.

Inasmuch as combination tannages are the rule, no recent practical results on leather made from a single tanning material are available. Most tanners, however, have had experience with the majority of the tanning materials listed and are in a position to judge whether the relative weight values are correctly placed. An article by Mr. Herbert W. Griffith on "The Comparative Efficiency of Certain Tanning Materials," published in the May, 1911, JOURNAL, gives a very complete and comprehensive report on a series of experiments carried out on a practical scale during or prior to the year 1901. Although since that time, conditions and processes of manufacture, together with methods of analysis, have undergone considerable change, and more or less influence the weight-giving values, the general characteristics of the various tanning materials no doubt remain relatively the same. It is therefore of interest to show Mr. Griffith's results on a practical scale as compared with results obtained in the laboratory. Considerable work has also been done by Dr. Paessler, the results

of which were published in 1910. No actual figures were given in the abstract printed in the June, 1910, JOURNAL, but the relative values are shown and will be included in the tables to follow.

In carrying out the experiment the writer proposes to make the present color test do double duty and serve as a weight test also. Sheepskin which has always given excellent results in this laboratory, was used and prepared as for the regular color test. Large pieces were then tacked out, allowed to dry in parchment form, cut in selected sizes and weighed. so that equal weights of dry hide contained approximately equal areas. These selected skins were then wet back and preserved as in the regular way. Various tanning extracts of known purity were then dissolved as for color tests, using 20 degree barkometer liquors, and the weighed skins entered first in weak measured solutions for 1 hour and then were put into the strong solution and allowed to stand 24 hours, after which they were washed, air dried, and again weighed. This weight was then corrected for the weight value per unit of tan as returned by the official method of analysis, and resulted in the following table, in which sulphite-cellulose extract is given an arbitrary value of 100.

TABLE I.

Tanning extract	Weight value per unit of tan.
Quebracho-unclarified	125.7
Chestnut	124.5
Myrobalans	122.8
Mangrove	120.8
Oak bark	120.6
Valonia	118.9
Hemlock	118.1
Sumac	115.1
Quebracho-clarified	114.0
Nut galls	112.9
Gambier	110.5
Sulphite-cellulose	100.0

These results should of course not be considered as constants for the various extracts as these figures are bound to vary with the raw materials and also with the different processes of manufacture,' but the general order even under these circumstances should not be materially changed. Of course these figures do not apply to results from the wheel, or drum tannage. A very impor-

tant factor, the acid-forming properties of the various extracts, is of course, of necessity, not considered. Most of the well-known acid-formers, however, are well up in the list. Another factor which seems to have considerable bearing on the weight question is the amount and character of insolubles present in liquors of tan-yard strength. The writer has always maintained in the case of quebracho at least, that a certain amount of insolubles in the proper form is an advantage, helping to make weight, and this seems to be borne out by the above results. However, certain natural disadvantages which manifest themselves to the tanner have led a great many to prefer the clarified article. With the exception of gambier, which deposits a large amount of insolubles, all the extracts which carry little or no insolubles are at the foot of the list.

Mr. Griffith's results are herewith shown in Table II.

TABLE II.

Tanning material	Per cent. gain in leather formation
Oak bark	105.6
Valonia	103.4
Oakwood extract	100.7
Chestnut extract	99.6
Quebracho extract	99.1
Hemlock extract	93.4
Myrobalans	75.6

At first glance no very great concordance is discernible, but on careful analysis the only marked discrepancy lies in the returns from the myrobalans. Just why this should be the writer is at a loss to explain unless the factor above referred to in regard to amount and character of insolubles has more bearing in the laboratory than in a practical way. With the exception of quebracho and chestnut, the relative order of the other comparable materials is practically the same. In the case of the quebracho this may in a measure be explained by the fact that the quebracho extract (unclarified) used by the writer in this experiment was one in which the amount and character of insolubles was such as to give the best possible weight results. At the time of Mr. Griffith's tests, quebracho extract manufacture was in its early stages, but even then its combining value as shown by Mr. Griffith in Table III was second only to oak bark. In the case of the chestnut, this difference may perhaps be due to difference

in locality, the chestnut used by Mr. Griffith in all probability coming from Europe, whereas the chestnut in Table I was our own American chestnut wood extract. It may be of interest here to quote Mr. Griffith's table of combining values, although as he says, the combining value does not necessarily indicate the weight-giving value.

TABLE III.

Tanning material	Combining value
Oak bark	100.4
Quebracho extract	100.0
Oakwood extract	94.6
Valonia	94.0
Hemlock extract	93.2
Chestnut extract	92.5
Myrobalans	78.8

Dr. Paessler's values referred to above are herewith given in Table IV and again the great discrepancy is shown in the myrobalans figure, Dr. Paessler agreeing with Mr. Griffith in this respect.

TABLE IV.

Weight-giving powers in order of value
Quebracho wood
Quebracho extract, not cold soluble
Mimosa bark
Oakwood
Chestnut wood
Oak bark
Pine bark
Mangrove
Valonia
Knoppern
Divi divi
Myrobalans
Sumac
Tannin
Cold soluble quebracho

It would therefore seem from the majority of opinions that the laboratory figure for myrobalans is incorrect and it may not be possible to use this test in this instance without some modification. The writer is hopeful, however, that further experiments may remedy this apparent inconsistency.

In view of the above results a table showing the relative price per pound of tannin, taken from one of the recent trade papers, may be of interest.

TABLE V.

Tanning extracts	Price per pound of tannin
Sulphite-cellulose	0.0357
Chestnut	0.0620
Quebracho-unclarified	0.0635
Mangrove	0.0671
Quebracho-clarified	0.0695
Myrobalans	0.0950
Oak bark	0.1000
Hemlock	0.1000
Valonia	0.1300
Sumac	0.1300
Gambier	0.1400

It might be well to explain that the above figures include the container.

Taking the writer's weight values per unit of tan, the following table shows the cost per weight unit of the various materials.

TABLE VI.

Tanning extracts	Cost per weight unit
Sulphite-cellulose	0.000357
Chestnut	0.000498
Quebracho-unclarified	0.000505
Mangrove	0.000555
Quebracho-clarified	0.000610
Myrobalans	0.000774
Oak bark	0.000829
Hemlock	0.000847
Valonia	0.001093
Sumac	0.001130
Gambier	0.001267

Quoting from Dr. Stockberger's paper, "The Production of New Tanning Materials in the United States" (January, 1910, JOURNAL). "Of the extracts used in 1908, chestnut and quebracho were the most important, together forming 74 per cent. of the total quantity reported for that year. The increase in the case of all other kinds was most apparent and was due largely to the greatly increased use of myrobalans and mangrove extracts."

Of course in selecting a tanning material, cost, color, and quality of leather produced are all considered, but it is interesting to note from the above figures how closely the tanner has followed Table VI in his selection.

METHODS OF OIL ANALYSIS.

By Charles Eachus.

As Chairman of a committee to revise methods of oil analysis in general, the writer presents his suggestions as to changes in these methods; and believes that methods of this sort, should be worded so that an analysis, carried out according to directions, would be rapid, easy of execution, and give results accurate enough for commercial purposes.

Taking the published methods in order, first comes *Saponification Value*. It would be a good idea to omit this test from the methods and not encourage its use, because it is of no value in the analysis of oils used in the Leather Industry. The *Saponification Value* gives a vague idea of the amount of unsaponifiable matter contained in an oil, but the straight determination of the unsaponifiable by shaking out with ether is as rapid and more accurate.

Acid Value.—A method, which gives accurate results for buying and selling oils reads as follows: Weigh 5 gr. oil into 8 oz. Erlenmeyer flask, add 25 cc. neutral ethyl alcohol, and boil with reflux condenser for five minutes. Add phenolphthalein and titrate till permanent pink with aqueous NaOH N/10. In the case of oils containing 50 to 90 per cent. free fatty acids, as in soap stock fatty acids, it is best to titrate with a normal alkali solution. Results are reported mostly as free fatty acids, instead of acid value which means nothing, and this method should be called the determination of free fatty acids, doing away with the term acid value.

Iodine Value.—For all ordinary oils the Hanus method gives accurate results, and it is the easiest of manipulation. Therefore it ought to be given preference in the methods of oil analysis. In the case of Chinese wood oil the Hanus method gives high and erratic results, which necessitates the use of the Hübl method for that oil.

Unsaponifiable Matter.—The most rapid and accurate methods are based upon the principle of saponification by boiling in a flask with alcoholic potash, and subsequent extraction of the unsaponifiable with ether. Boiling one hour will saponify most oils

without shaking the flask, but it is more difficult to saponify solid fats. The addition of 25 cc. petroleum ether, and a few glass beads in the flask causes an agitation, which does away with shaking the flask. The best condenser for boiling this solution is the one connected with Landsiedl's extraction apparatus, which is supplied by Eimer and Amend. Aqueous KOH is used, because it keeps better than alcoholic KOH. The writer suggests as follows: Weigh 5 grams oil or fat into 8 oz. Erlenmeyer flask, and add 5 cc. aqueous potash solution (50 grams KOH dissolved in water and diluted to 100 cc.). Then add 45 cc. alcohol, 25 cc. petroleum, ether boiling at 70° C., and a few glass beads. Boil one hour, or more with reflux condenser. Wash contents of flask into a 500 cc. separatory funnel, using both water and ether. Cool solution and shake three times with petroleum or sulphuric ether, using 50 cc. each time and shaking a few minutes. Use alcohol to break emulsions, and combine ether solutions in another separatory funnel. Wash the ether solution by shaking three times with 50 cc. water and 10 cc. neutral alcohol, using alcohol to break emulsions. Finally transfer ether solution to a beaker and heat on water bath, or in steam oven for five minutes. Pour ether solution into a weighed No. 1 beaker, evaporate to dryness, dry at least five hours longer, and weigh unsaponifiable. In the case of moellon degras and degras products use sulphuric ether, but with other oils and fats use petroleum ether.

Maumene Test is of no use and should be omitted.

Specific Gravity.—The writer would advise that the determination of specific gravity be taken at a temperature within five degrees of 15.5° C., and calculated to specific gravity at 15.5° C. The Westphal balance should not be relied upon, unless it is standardized with a specific gravity bottle. A good standard would be the 50 cc. specific gravity bottle with thermometer and capillary overflow.

Titer Test.—This is a very easy test and is usually made by boys in the larger oil and grease laboratories. It is important to a certain extent in the leather business, where tallow is bought on titer. Therefore it might as well be published. The method

is described very well, although the description is somewhat voluminous, in the A. L. C. A. methods.

Melting Point.—In the various books on oil analysis, no definite method of determining melting point is recommended. The writer finds that the most commonly used method is the one based upon the principle of drawing some of the melted grease into a capillary tube, letting it cool, and then immersing it alongside of a thermometer in a water bath, which is heated, until the grease melts and rises up the capillary tube. The writer has found this a reliable method for all greases, except paraffin, and the solidification point of paraffin is best determined by the English method, given in Lewkowitsch. The paraffin is melted in a test tube, and then a titer test thermometer is used to stir the melted paraffin, until the temperature ceases to fall, remains stationary a few minutes, and the paraffin solidifies. In the melting point determination for greases given above, the diameter of the capillary tube and time of cooling the melted grease in the tube have little effect upon the melting point, but this might be investigated by the incredulous.

Cold Test.—In this test the writer would recommend letting the frozen oil stand five minutes in the freezing mixture, instead of one hour. The test as given is very indefinite and inaccurate, and should be discountenanced in favor of cloud test.

Cloud Test.—This test as directed gives accurate results, which indicate something of value in practice.

MOELLON DEGRAS.

Moisture.—An accurate method for this determination is to weigh 5 grams into a platinum dish, or crucible, heat over small bunsen flame until bubbling ceases, and oil begins to spit and smoke slightly. Cool and weigh. The loss is moisture. The residue can be burned and ash determined.

Unsaponifiable.—This is determined by the same method that is used for other fats. Sulphuric ether should be used to extract the unsaponifiable. The nature of the unsaponifiable gives a good idea of its composition, and it can be examined by chemical tests for wool grease, mineral, and rosin oils.

Degras Former.—The soap solution from the unsaponifiable is evaporated to a paste so that nearly all the alcohol is expelled, and then diluted to 200 cc. with water and brought to a boil in a No. 3 beaker. Concentrated HCl is added in slight excess, (about 25 per cent. more than enough to neutralize total alkali). Contents of beaker are boiled gently one-half hour and poured into a 500 cc. separatory funnel. When cool, the acid solution is drawn out of separatory funnel and thrown away. About 100 cc. water is poured into the beaker used originally for the separation of the fatty acids, and brought to a boil. This is poured into the separatory funnel to wash the beaker and funnel. Fifty cc. of 86° gasoline is used to wash the beaker, and this is then poured into the separatory funnel after cooling to dissolve unoxidized fatty acids. The water and gasoline solutions are run out of the funnel and thrown away. This process of washing the beaker and funnel with water and gasoline is repeated twice, and finally the oxidized fatty acids, or degras former, are dissolved in hot ethyl alcohol, filtered, evaporated to dryness, and weighed.

The combined gasoline solutions can be washed with water, evaporated and weighed to determine unoxidized fatty acids.

The free fatty acid is determined as usual.

The iodine value and hide fragments are determined by methods given in Lewkowitsch, but these determinations are not of sufficient importance to justify publishing special methods.

SULPHONATED OILS.

The increasing sale of sulphonated oils demands some uniform and accurate methods of determining the value of these oils. The determinations of water and unsaponifiable give definite results, but other chemical tests do not indicate as much as practical emulsion tests.

In the manufacture of a sulphonated oil, whether the sulphonation is accomplished with sulphuric acid, or with benzol sulphonic acid, Twichell's reagent, etc., the resultant product is a mixture of water, unsaponifiable, free fatty acids, sulphonated fatty acids, soaps, glycerine, unaltered oil, and mineral matter. Some of these determinations are important, and may be considered as follows:

Water.—Small amounts of volatile matter, other than water, are lost by heating or drying sulphonated oils, but the writer finds that elaborate methods like distillation with xylol, are no more accurate than simple drying methods. The platinum crucible method does not give very close results, and all ammonia is driven off by that method. However the percentage of ammonia in these oils is seldom over 0.5 per cent. The sand method is fairly accurate, but the writer has obtained best results by weighing 2 grams of well mixed oil into a crystallizing dish 3-inch diameter, and heat in steam oven two hours. Cool in desiccator, weigh, replace in oven, and weigh three more times at intervals of two hours. The chance for gain or loss by oxidation or volatile matter in these oils is slight. They contain over 10 per cent. of oxidized fatty acids through oxidation in the process of manufacture and these affinities are satisfied.

Unsaponifiable can be determined as in other oils.

Unaltered oil can be accurately determined as in Lewkowitsch, but the writer prefers to do as follows: Weigh 10 grams in Erlenmeyer flask, add 50 cc. alcohol, boil reflux five minutes and titrate with normal NaOH till permanent pink. Then wash into separatory funnel and extract unaltered oil with petroleum ether as in unsaponifiable.

Sulphonated Fatty Acids.—The method given in Lewkowitsch gives uniform and accurate determinations of combined SO_3, but it is a question whether the sulphonated fatty acids of a cod oil can be calculated from this as they are calculated in case of sulphonated castor. At present the writer prefers to report results as combined SO_3, instead of sulphonated fatty acids. Lewkowitsch, Vol. III, page 155, states that a sulphonated castor oil can be resolved into two portions by shaking with ether, and washing with water. The same process applied to a sulphonated cod oil gives interesting results. From this procedure as a beginning the writer has formed definite opinions as to the content of sulphonated fatty acids in an oil, and as to whether the free fatty acids reported in the analysis of a sulphonated oil are really free fatty acids, or due to the saponification of sulphonated fatty acids.

Total Fat.—The writer could get no accurate results with Benedikt's method as given in Lewkowitsch, because in the case

of sulphonated cod oil, the free fatty acids will not mix with the paraffin, but stay as a sticky mass on the bottom of the paraffin. The separation of the fatty acids from the soap solution in an unsaponifiable determination yields a product that is very difficult to handle.

The simple method of Finsler-Breinl by separation of the fatty acids in a 250 cc. flask, and measuring them in the graduated neck of the flask works very well with castor oil, because the sp. gr. of the fatty acids is known and they contain no mineral oil. By applying this method to a sulphonated cod oil, the writer found 72.60 per cent. of total fat. The sp. gr. of the fatty acids in another determination with larger quantity was found to be 0.9476. By Herbig's method described below the total fat obtained in four determinations was 73.01, 73.80, 73.26, 73.86.

The method is as follows: Ten grams of oil are mixed with 50 cc. water in flask till dissolved, and the solution then mixed with 25 cc. of dilute HCl (1-5) and boiled five minutes. When cold the contents of the flask are transferred to a separatory funnel with water and well shaken with 100 cc. sulphuric ether. It is well to repeat the shaking with another 100 cc. ether. The ether solution is washed with water and finally evaporated in a tared beaker as in unsaponifiable. In determinations by this methods the fatty acids after drying 24 hours showed no loss in weight.

These fatty acids also contain the unaltered oil, which contains some glycerine, but it will be fairly uniform, as the unaltered oil in sulphonated cod oils usually runs from 20 to 25 per cent., excluding mineral oil.

The sulphonated cod oil in which these determinations of total fat were made showed the following analysis:

	Per cent.
Moisture	22.01
Unsaponifiable	0.18
Unaltered oil	25.38
Ash	2.81

If the moisture and ash are added together and subtracted from 100 per cent. the remainder is 75.18 per cent. Allowing for a

small amount of glycerine, and impurities, the total fat in this sample must have been close to 73 per cent.

Emulsification Tests for Sulphonated Oils.—Practical emulsification tests for these oils indicate more than chemical analyses, because an oil showing a poor chemical analysis can be treated so as to make a first class emulsion.

Emulsions made in a laboratory should follow tannery practice on a small scale, as much as possible. Sulphonated oils are used in tannery practice in admixture with water alone, and on a larger scale mixed with other oils to emulsify them. The writer cannot get any definite results from simply shaking the oils with varying amounts of water and watching the emulsions, because the same oils work differently at different times. As these oils are used chiefly for emulsifying other oils, an emulsion made in the laboratory, by shaking the sulphonated oil with some other oil and water is nearer practice, and gives more concordant results.

A laboratory test can be worked as follows:—Mix thoroughly 25 per cent. of sulphonated oil with 75 per cent. of either mineral oil or neatsfoot oil, add a given amount of water, from 2 to 10 times the weight of oil. The mixture should be at least 200 cc. and shaken in a bottle in the non-tannin shaker for 30 minutes.

Then pour the emulsion into a graduated cylinder and note the amount of separation. The writer calculates the percentage of oil separated, from total oil taken, at different intervals. In using mineral oil an oil of the same gravity should be taken each time. Mr. W. S. Loud using a test similar to this gets best results with a 25° Baumé mineral oil. Some sulphonated oils tested this way will show no separation of free oil in boiling hot solution in 24 hours, but others will separate in a few minutes. Of course in tests of this kind too much is left to the judgment of the individual, and a test giving a definite, uniform result is to be preferred.

THE ACTION OF ACIDS ON HIDES.[1]

By Henry R. Procter.

Recent investigations have thrown a good deal of light on the nature of the combination formed by acids with hide, and the problem may be regarded as a first step to a complete understanding of the theory of tanning in general. There is no longer any doubt that an actual compound is formed, of the nature of a salt in which hide acts as a weak base; and a hide swollen with sulphuric acid is a sulphate of hide, just as bluestone is a sulphate of copper. Now sulphate of copper is a perfectly definite compound containing always exact proportions of sulphuric acid and copper, while according to the quantity and concentration of acid used, a hide may be more or less swollen and contain acid in greater or less proportion; and at first sight, this seems a fatal objection to regarding the swollen hide as a true compound.

The reply to the objection is two-fold. Firstly, hide is a very weak base, and therefore its compound is easily hydrolyzed or decomposed by water. The same thing happens with all salts of weak bases when in solution. We all know that an alum solution tastes sour as well as astringent, and the reason is that a certain proportion of the salt is decomposed by the water, and there is actually a portion of free sulphuric acid, and a portion of uncombined alumina present together in the liquid; and the larger the proportion of water, and the greater is this dissociation. Now the same thing is true of hide in a still greater degree, since hide is a weaker base than alumina, and thus in a weakly swollen hide there is always a good deal of uncombined hide. With more concentrated acid liquors, the free acid increases in the hide, and the uncombined hide-substance diminishes; while with enough water it is possible with time and perseverance to wash most of the acid out.

The second part of the explanation is, that in order to prevent the combined acid from washing out, there must always be a certain quantity of free acid also present. This quantity follows a quite definite law, but the exact nature of this law is too complex for explanation here. Every swollen hide is thus a system of hide-salt, free acid, uncombined hide, and water, and

[1] *Shoe and Leather Reporter*, March 20, 1913.

each of these bears a quite definite relation to the strength of the solution in which the hide is swollen. If the object of the tanner is to swell the hide, he desires that the hide should contain as large a proportion of water as possible, and with strong acids like sulphuric or hydrochloric this is attained either by swelling in a very weak solution, or still more effectively, by first treating with a somewhat stronger acid, and then suspending in clean water. A little of the acid will come out, but a much larger proportion of water will go in. The same rule applies in soaking with acids:—24 hours in dilute acid and 24 hours in water will soften more than 48 hours in the acid alone; and a very dilute acid, if the water treatment is not adopted, will usually soften more than a more concentrated one. With naturally weak acids like acetic or butyric, this rule no longer holds good, for reasons which are known, but which cannot be explained here.

Of course a consequence of what has been said, is that a point is reached, very soon with strong mineral acids, and more slowly with the weaker organic, at which the hide is practically "saturated" with acid, and will take no more except as loose free acid in its pores, and as acid in this form does not swell, is generally injurious, and costs money, it is well to avoid it. The largest quantity of acid which can be fixed is about 1 gramme-molecule for each kilo of *actual dry hide substance,* which in non-chemical terms amounts to about 3½ per cent. of actual (dry) hydrochloric acid, or 5 per cent. of the most concentrated sulphuric; and something near this amount is taken up from very dilute solutions. As ordinary wet hide does not contain more than 20 per cent. of dry substances, a quantity of 1 per cent. of sulphuric acid is about all which can be taken up, and if not more than this quantity is used *as a maximum,* nearly the whole will be absorbed by the hide if it is suspended in water containing it for 24 hours. Of course for many purposes much less may be enough, but if reasonable time is given the quantity of acid should be reckoned on the weight of *hide,* and not on that of *water.* Of course if hides are limy, allowance must be made for the acid which will combine to form gypsum.

When a swollen hide is tanned, there are still many gaps in our knowledge of what occurs, but it is certain that the combined acid is gradually driven out by the tannin—a pickled skin may be

so completely tanned that no sulphuric acid can be found in the finished leather, though this is by no means always the case, and if acid remains in, the durability of the leather is impaired; and if of hemlock tannage, it ultimately becomes brittle or tender, and suffers a sort of "red decay."

There is no doubt that acid swelling slows the tannage at the outset, though it often leads to a heavier leather. Whether the finished leather can be regarded as a salt of hide and tannin is still very doubtful, though there is much for the view that such a compound is formed. If, however, this is really true, it is much complicated by other effects. The physical effect of swelling, whether by acids or alkalies is to split up the fiber-bundles unto their constituent small fibrils, and thus enormously to increase the area of the internal surfaces of the hide; and a large part of the tanning of heavy leathers consists in the coating of these surfaces with "reds," "bloom," and other scarcely soluble matters, which add greatly to the weight and solidity of the leather. Such coating of surfaces is generally called "adsorption," but the word does not add much to our knowledge, and probably covers a variety of causes, partly chemical, and partly dependent on such physical matters as solubility and surface-tension.

Another complication which will have to be studied before the effect of acids in tanning can be fully explained is that of their action on the tannins themselves; and this varies with the particular tannin and the particular acid far more than their effect on hide, which is mainly due to their acid character. It may be noted especially that sulphuric acid is always destructive to tannins, and its use in extracting tanning material for extracts has been shown to increase the non-tannins and diminish the tannins in the product, though it frequently brightens color.

As has been said, a swollen hide goes into the liquors as a salt or compound of the acid used in swelling, and while we know something of the effect on tanning of a given degree of swelling, we do not know whether it matters whether we tan a sulphate, chloride, or acetate. The problem may be commended to our younger leather chemists, but is not an easy one.

THE QUANTITATIVE DETERMINATION OF THE FALLING OF SKIN IN THE PUERING OR BATING PROCESS. PART II.[1]

By Joseph T. Wood, Henry J. S. Sand, and Douglas J. Law.

In a former paper (*J. S. C. I.*, March 15th, 1912; *J. A. L. C. A.*, May, 1912) we gave an account of an apparatus which we may describe as a puerometer for the measurement of the amount of depletion which skins undergo in the process of puering, It is illustrated in Fig. 1.

In the present paper we give some of the results obtained by means of the apparatus and also some considerations of the best way of expressing these results.

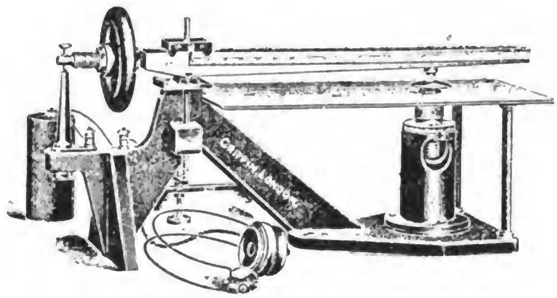

Fig. 1.

In carrying out the tests, it was found desirable to examine first of all the condition of the skin before entering the puer liquor, and in this way the apparatus proved of great use in showing the degree of plumping the skins had received during the liming or preparatory processes, and of equal use for this purpose as for the original purpose for which it was designed.

What we determine is the amount of compression undergone by the skin under a certain load which must be so chosen that it does not cause rupture. There was however no danger of this in any of our experiments. In our apparatus the load is distributed over a section of one square centimeter, the diameter of the circular jaws being 1.128 cm. The machine thus indicates directly the specific load or stress p undergone by the skin. The

[1] *J. Soc. Chem. Ind.*, April 30, 1913, XXXII, 398-402.

latter is compressed from its original thickness l_1 to a new thickness l_2, the relative compression thus being

$$\lambda = \frac{l_1 - l_2}{l_1}.$$

We propose to refer to the number E, defined by the equation

$$E = \frac{p}{\lambda}$$

as the average resistance of the skin to compression under the stress p. It may be taken as a measure of the firmness of the skin.*

When a skin is subjected to successive increasing loads, and the load removed each time, it is found that even under a very small load it does not as a rule entirely recover its original thickness, but that a certain amount of set or permanent compression takes place. The difference between the total and the permanent compression is the elastic compression, and we propose to measure the resilience of the skin by the percentage ratio of the elastic to the total compression.

To understand what takes place during the compression of wet skin in our apparatus we may consider the skin to be of the nature of a sponge, the walls of which have varying degrees of firmness, elasticity, and thickness according as the skin is in the limed, the delimed, or the puered condition. The volume compressibility is probably negligible in all cases, but a certain portion of the skin substance always flows under pressure beyond the jaws of the machine. The principal effect of putting pressure on the skin is to diminish the size of the interstices or cavities in it with concomitant expulsion of water. The role played by the water as such is only to slow down the process of compression: it should not affect the final equilibrium. As the skin is perfectly wet, and, whether examined under water or not, must be considered completely surrounded by water, the surfaces of contact between water and skin-fiber are not affected to any appreciable extent by the experiments, and so capillarity plays practically no part in them. It is obvious that the size of the jaws will be of the very greatest importance in determining the time taken to attain equilibrium, since with large jaws there is little opportunity

* If the skin were perfectly elastic E would be the modulus of elasticity.

for the water to escape along the edges. Besides, the flowing of the skin as such will probably be hindered to so great an extent by large jaws that it is doubtful whether, even with the proportionately heavier loads required to produce the same stresses, as great compression will be obtained with large as with small jaws. The size of the jaws should therefore be specifically stated in experiments on the compression of skin. Professor Procter has suggested to us that the flow of water from the skin might be very greatly facilitated by placing a circular disc of it between pieces of porous tile in a tube under water, and that the flow of skin substance might in this way be inhibited. We propose to revert to this suggestion in our future experiments.

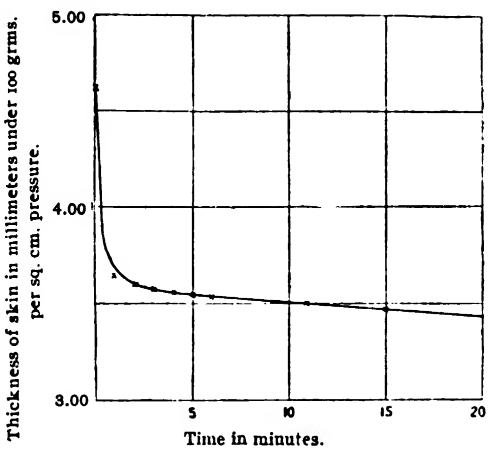

Fig. 2.

In the experiments we have carried out with the skin in air, we have usually allowed three minutes for each reading. Fig. II, shows diagrammatically the effect of time on the compression of a limed skin. It will be seen that after three minutes over 90 per cent. of the final compression at 20 minutes was reached. A much larger period than 20 minutes cannot be taken, owing to the gradual drying of the skin.

When the pressure is released from the skin, elasticity will tend to restore it to its former shape and thickness. If this is done in air it will result in very greatly increasing the surfaces of con-

tact between water (wet skin fiber) and air, and will therefore be very much opposed by forces of capillarity. In order to avoid this, the experiments must be carried out under water. We therefore now perform all our experiments on resiliency under water. In compression experiments it is also advantageous to work in this manner, as the flow from the skin is thereby facilitated and surface effects generally eliminated. The final results are however not affected appreciably. We take this opportunity of expressing our great indebtedness to Professor Procter, at whose suggestion we first carried out experiments under water.

We have also carried out experiments with 20 per cent. gelatin. Here there is no expression of water, and as the volume compressibility of gelatin is quite negligible the diminution of thickness is completely compensated by bulging out at the sides. Owing to the absence of pores, the gelatin, as was to be expected, is very considerably firmer than any of our skins under the pressures we have employed. It is also almost completely, resilient, and the value of E approaches constancy as with a perfectly elastic body. As in similar experiments on the elasticity of other substances, it is not to be expected that the size of the jaws will very appreciably affect the relation between compression and specific load. We have found that the results are very greatly improved by allowing the gelatin to set between the jaws of the machine: all errors due to uneven contact of the jaws which are very noticeable under small compression thus disappear. We have also found that the firmness of the gelatin very appreciably increases for some time after setting. Thus a 20 per cent. gelatin jelly gave a value of 1,070 grams per square centimeter for E immediately after setting, but 18 hours after setting a value of 1,790 was obtained under similar conditions. Table 1 shows the behavior of two different jellies set between the dies of our machine. After each compression, the load was released and the resulting thickness l_3 measured. The resilience R was then calculated.

The experiments on gelatin are interesting, as affording an indication of the probable behaviour of the "jelly water" in a skin to which its elasticity is probably mainly due. As is known, the experiments of Hardy, Bütschli, and others have shown that a

gelatin jelly consists of two distinct phases, the one richer, the other poorer in gelatin. According to the "emulsoid" theory, each of these phases in its turn is a very fine emulsion of two distinct liquids; elastic deformation would thus be equivalent to the deformation of the spherical drops of the emulsion. These would recover their shape after removal of the stress owing to the forces of capillarity. A similar explanation would hold for the behaviour of the jelly-water in a skin.

Our experiments on the compression of skins have yielded the interesting result that above loads of about 100 grams per square centimeter the values of E are approximately linear functions of the stresses, *i. e.*, E can be approximately expressed as a function of the load p by an equation of the form.

$$E = ap + b$$

in which a and b are constants. Tables 2 to 11 contain the results of numerous experiments on limed, puered, and delimed skins, and Fig. III, represents these same results graphically. At lower pressures than 100 grams square centimeter the values of E usually fall off more rapidly than corresponds to the simple linear relation. If however we accept the view that these results are vitiated by imperfect contact of the jaws—a view which derives some support from the experiments on gelatin described above, and also from the fact that results more nearly approximating to the linear relation are obtained in experiments carried out under water—we may then by a simple process of extrapolation calculate values of E corresponding to very small loads. Thus the constant b, which is the value of E corresponding to a zero load, may be easily found from our experiments, *e. g.*, by subtracting the difference between the values of E at 200 and 100 grams per square centimeter load from the value of E at 100 grams per square centimeter. We may call the value so found the firmness of the skin under zero load, or perhaps—if we adopt the view that the skin approaches a state of true elasticity at very small loads—the modulus of elasticity of the skin. The other constant, a, characterizing the behaviour of the skin, may be readily found from our experiments, *e. g.*, by dividing the difference between E at 200 and E at 100 grams per square centimeter by 100. We may say that for a limed sheep-skin E measured under a load of 100

grams per square centimeter approximates to a little more than 400 grams per square centimeter, for a well-puered sheep-skin under the same conditions to 170 grams per square centimeter. For a delimed sheepskin, E measured under these conditions is usually slightly lower than for a puered skin. The values of *b* for a puered sheep-skin usually vary between about 20 and 60 grams per square centimeter according to the amount of puering the skin has undergone, for a limed skin they usually lie between 200 and 400 grams per square centimeter, and for a delimed skin between 50 and 100 grams per square centimeter.

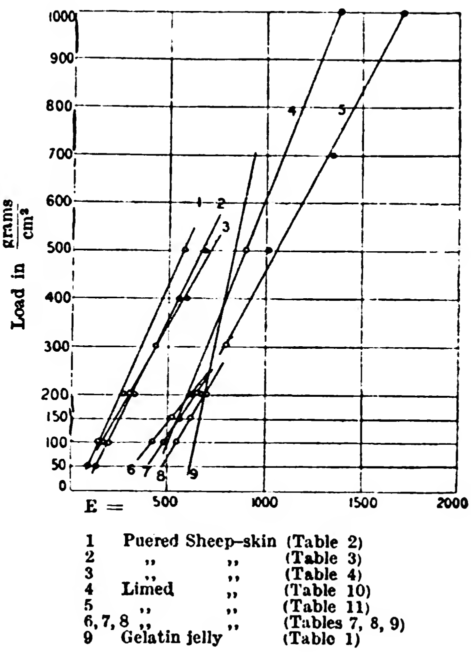

Fig. 3.

Professor Procter has suggested to us that the compression of the skin may be determined by a law to the effect that the amount of interfibrillary water expelled by each increase of pressure will approximate to a uniform proportion (percentage) of the remaining volume of water. In addition to this, there will be a certain amount of compression due to the deformation of the skin

substance and depending on the jelly water, and this compression will probably be simply proportional to the load. These assumptions lead to the equation

$$l = f + ae^{-C_1 p} - C_2 p$$

in which l is the thickness of the skin under the pressure p, f is the volume of fiber substance plus jelly-water per unit surface of skin under zero load, a the volume of the interfibrillary water under the same conditions, $a + f$ thus the thickness of the skin under zero load, $e = 2.718$ the base of the natural logarithms, and C_1 and C_2 constants governing respectively the compression due to the expulsion of interfibrillary water and to the deformation of the skin substance. It is very doubtful, however, whether an equation of the above form will express the results obtained by us so far, as well as the empirical relation enunciated above.

The resiliency of the skin was always determined under water as explained above. For this purpose a small brass capsule was prepared which could be mounted on the lower jaw of our machine and into which an auxiliary jaw of 1 square centimeter surface protruded. Table 12 expresses the results obtained. It will be seen that, measured under these conditions, the resiliency of puered roan is about 20 per cent., that of a limed sheep-skin between 70 and 80 per cent., and that of a delimed sheep-skin also about 20 per cent.

The behaviour of delimed skins, which, as explained above, are slightly less firm than puered, under a pressure of 100 grams per square centimeter caused us some surprise. To further elucidate this matter we have carried out the following experiments. By the examination of eight different skins first in the delimed and then in the puered condition we have found that the water-content in both stages of manufacture is practically identical: thus in one case we obtained for delimed skin 83.9 per cent., for puered skin 84.2 per cent. water. That the ash-content of a skin increases during puering and is greater than that of a well-delimed skin has already been stated in Wood: The Puering, Bating, etc., of Skins, p. 38.

On soaking the delimed and puered skins in 96 per cent. alcohol for 2 days and again making a test the values obtained were, for 100 grams per square centimeter

Delimed skin E = 490
Puered skin E = 251

which is the proportionate difference we expected between the two skins.

With regard to the differences in the results obtained for different parts of the same skin, we find that the variations are very much of the same order as those found for the breaking strain of leather by Professor Paessler,* and this fact must be borne in mind in using the method. The simplest way is to take samples from the neck and butt of the skin. The thickness found will enable one to judge if the piece taken is about the average. Pieces too thick or too thin should be rejected. In practice it is well-nigh impossible to give attention to each individual skin. If therefore two skins are taken, one representing the firmest and the other the softest, the comparison of the figures obtained is very often of great use.

In conclusion we wish to draw attention once more to the original object of the research, which was to devise a method for expressing *numerically* the amount of depletion undergone by skins in the puering process, so as to make records for future reference and comparison.

TABLE I.

Twenty per cent. (about) gelatin jelly set between dies of machine (2-minute intervals).

p	l_1	l_2	l_3	$\lambda = \frac{l_1 - l_2}{l_1}$	$E = \frac{p}{\lambda}$	Resiliency R per cent.
10	3.39	3.37	3.40	0.0089	1125	100
20	3.39	3.34	3.40	0.0149	1340	100
50	3.39	3.25	3.39	0.0415	1210	100
100	3.39	3.12	3.37	0.0800	1250	93
200	3.39	2.92	3.34	0.1390	1440	90
300	3.39	2.69	3.23	0.2060	1450	77
Twenty per cent. gelatin jelly (another sample of gelatin).						
10	4.24	4.18	4.25	0.0142	705	100
20	4.24	4.11	4.24	0.0307	650	100
50	4.24	3.89	4.24	0.0825	610	100
100	4.24	3.39	4.20	0.200	500	95
200	4.24	3.00	—	0.294	680	—
300	4.24	2.52	3.91	0.405	740	81

* Ueber Reissfestigkeit bei Riemenleder. *Collegium*, 1909, 45, etc.

TABLE 2.

Puered Sheep-skin.

Load in grams cm^2	l_1	l_2	λ	E
0	2.710	2.710		
5	2.710	2.155	0.205	24.5
10	2.710	1.950	0.280	35.8
15	2.710	1.700	0.373	40.3
20	2.710	1.305	0.518	38.6
25	2.710	1.250	0.539	46.5
30	2.710	1.185	0.566	53.0
40	2.710	1.125	0.585	68.5
50	2.710	1.070	0.605	83.0
60	2.710	1.015	0.625	96.2
70	2.710	0.980	0.638	110
80	2.710	0.920	0.660	122
90	2.710	0.875	0.677	134
100	2.710	0.795	0.706	142
200	2.710	0.645	0.762	263
500	2.710	0.360	0.867	578

TABLE 3.

Roan Puered in Artificial Bate.

Original thickness $l = 2.64$.

p	l_2	λ	E
0	2.64		
5	2.25	0.1734	28.83
10	2.02	0.2348	42.59
15	1.84	0.3030	49.51
20	1.71	0.3523	56.78
30	1.60	0.3940	76.15
50	1.46	0.4470	111.9
75	1.33	0.4963	151.1
100	1.24	0.5304	188.5
200	1.01	0 6176	323.8
300	0.92	0.6516	460.5
400	0.82	0.6896	580.1
500	0.69	0.7388	677.0

TABLE 4.

Roan Puered.

Original thickness $l = 2.56$ mm.

p	l_2	λ	E
0	2.56		
5	1.98	0.2265	22.08
10	1.74	0.3203	31.22
15	1.56	0.3906	38.41
20	1.44	0.4376	45.71
30	1.34	0.4766	62.95
50	1.16	0.5470	91.41
75	1.06	0.5860	128.00
100	0.98	0.6173	162.00
200	0.85	0.6680	299.4
300	0.70	0.7267	428.7
400	0.47	0.8165	490.0

TABLE 5.

Puered roan.

p	l_1	l_2	l_3	λ	E	R (resiliency) Per cent.
50	2.46	1.59	1.69	0.355	141	11.5
100	2.46	1.32	1.40	0.460	217	7.4
200	2.46	1.17	—	0.520	385	—
300	2.46	1.07	—	0.564	530	—
100	1.88	1.13	1.23	0.400	250	13.4

TABLE 6.

Limed Sheep-skin.

Load in grms. cm^2	l_1	l_2	λ	E
0	4.475	4.475		
5	4.475	4.305	0.0380	132
10	4.475	4.255	0.0492	205
15	4.475	4.185	0.0684	220
20	4.475	4.095	0.0849	236
25	4.475	3.985	0.109	230
30	4.475	3.900	0.128	235
40	4.475	3.760	0.160	250
50	4.475	3.615	0.192	260
60	4.475	3.535	0.210	286
70	4.475	3.445	0.230	305
80	4.475	3.385	0.243	330
90	4.475	3.300	0.262	344
100	4.475	3.215	0.282	355
200	4.475	2.635	0.411	487
500	4.475	1.955	0.563	890
1,000	4.475	1.255	0.719	1,400

TABLES 7, 8, 9.

Limed Sheep-skin.

p	l_1	l_2	λ	E
100	3.91	2.98	0.238	420
150	3.91	2.78	0.289	519
200	3.91	2.56	0.319	625
100	2.33	1.90	0.184	542
150	2.33	1.76	0.244	613
200	2.33	1.66	0.287	695
100	5.98	4.71	0.212	471
150	5.98	4.37	0.269	557
200	5.98	4.09	0.316	635

TABLE 10.

Limed Sheep-skin, a different portion taken for each pressure.

p	l_1	l_2	l_3 (thickness on removing load)	R (resiliency) Per cent.	λ	E
20	4.80	4.30	4.59	58.0	0.104	193
30	4.36	3.90	4.18	60.8	0.105	286
40	4.93	4.24	4.64	58.0	0.140	353
50	4.88	4.09	4.66	72.1	0.162	310
60	5.04	4.11	4.67	60.2	0.184	308
70	4.77	3.87	4.40	58.9	0.190	372
80	4.82	3.58	4.23	52.4	0.258	315
90	4.65	3.44	4.04	49.6	0.260	345
100	4.48	3.41	4.04	58.8	0.240	420
200	4.42	2.99	3.69	49.0	0.325	620
500	5.46	2.38	3.03	21.1	0.565	890
1,000	4.89	1.34	1.68	9.6	0.725	1,380

TABLE 11.

Limed Sheep-skin, all pressures on same portion.

p	l_1	l_2	l_3	R Per cent.	λ	E
20	3.61	3.27	3.45	52.3	0.093	216
50	3.61	3.09	3.38	55.7	0.144	481
100	3.61	2.85	3.27	55.0	0.210	637
200	3.61	2.49	3.02	47.5	0.310	839
300	3.61	2.25	2.80	40.5	0.376	1,176
500	3.61	1.81	2.32	28.4	0.497	1,414
700	3.61	1.72	2.22	26.5	0.521	2,700
1,000	3.61	1.48	1.82	31.0	0.590	3,000

TABLE 12.

Limed Sheep-skin, under lime water.

p	l_1	l_2	l_3	λ	E	R Per cent.
100	3.13	2.26	2.87	0.278	360	70.0
100	3.34	2.39	3.20	0.285	350	85.0
		Puered Sheep-skin, under water.				
100	1.79	0.76	1.06	0.575	174	29.0
100	1.79	0.77	0.95	0.570	175	17.4
		Delimed Sheep-skin, under water.				
100	3.52	1.50	1.82	0.572	174	15.8
100	1.79	0.91	1.15	0.490	205	27.3

DISCUSSION.

MR. S. R. TROTMAN suggested that the authors' method of testing might prove useful in the examination of glue and gelatin, which at present were generally judged by the percentage of water they were capable of absorbing.

MR. C. E. B. MERRIMAN inquired what would be the result of the tests if carried out in a vacuum.

MR. J. H. DUNFORD pointed out that different mechanical tests for glue often yielded different results. Thus he had known cases where a glue which was found stronger than another by the shot test gave a weaker joint than the other.

MR. J. M. WILKIE inquired what was the percentage error of the tests.

MR. S. J. PENTECOST inquired what was the effect of oil and grease on the mechanical properties of the skin.

MR. J. T. WOOD, in reply, said that beyond causing rapid evaporation of the water contained in it the effect of placing a puered skin in a vacuum would be slight. He had, however, suggested puering in vacuo, as this would be favorable to the depletion of the skin. It was not possible to obtain exact duplicates of any test, since the test must necessarily be made on different parts of the skin. Adjacent pieces did not differ more than a few per cent., the third figure of E being unreliable. Natural fat in a sheep-skin in some cases added much to its thickness, and care must be taken in selecting test pieces where the fat was normal. In a puered skin the fat was set free and the effect was negligible.

ABSTRACTS.

A New Clarifying and Decolorizing Agent for Tanning Extracts. Leopold Pollak. *Collegium*, 1913, 84-6. The firm Edmund Dammer, Duisburg, has lately manufactured two preparations, Mark I and Mark II, containing 7.56 and 6.72 per cent. N respectively. Mixed with water, they give emulsions, most of the nitrogenous matter going into solution and not coagulating on boiling, but giving ppts. with weak acids and salts. The author tested the efficiency of these agents for clarifying chestnut and oak extracts and finds that a minimum red (Lovibond tintometer) was attained with addition of 0.2 per cent. reagent to 3 per cent. liquors; 0.4 per cent. gave slightly less but would not repay the additional expense. Yellow components were not lowered nor is this required in practice. Mark I appeared to have 5-7 per cent. more action than Mark II.

When tubs are used for clearing, heat should be used; clearer liquors are obtained by cold treatment but the loss of tannin is greater. When used solid, the powder is added to the fresh wood in the diffusor in amount equal to 0.2 per cent. of the final liquor. On boiling, large flocks are formed which settle readily on cooling. To use in solution, which is less convenient, the procedure is like that of the Gondolo process. The agent is mixed with water at 35° to a paste and this stirred into the liquor previously cooled to 45°. The whole is then warmed to 65° and finally let cool to 15° and settle.

	Chestnut wood liquor		Oak wood liquor	
	Before clearing	After clearing	Before clearing	After clearing
Soluble tans	3.5	3.2	2.5	2.2
Soluble non-tans	1.1	1.0	1.2	1.1
Insoluble	0.14	0.06	0.2	0.04
Yellow, Lovibond	15.7	13.4	23.5	19.3
Red, Lovibond	4.1	3.0	7.7	5.7
Gravity, Bé.	3.15	2.7	2.2	2.1

These results are not inferior to those with blood, and the process is preferable for its cleanliness and stability of reagent, an advantage in warm latitudes. Extracts of myrobalans, sumac and pine may be similarly clarified. For quebracho the advantages are less, but if used, the second method is best. W. J. K.

Natural Organic Acids in Chestnut Wood Extract. Leopold Pollak. *Collegium*, 1913, 86-8. These results obtained some three years ago are thought to be of interest in connection with Jedlicka's work on the acids of oak wood (ante p. 169).

Fresh chestnut wood (air dried) contains 0.06 to 0.075 per cent. volatile acids (computed as acetic). Leached wood (after drying) contains also

only 0.06-0.09 per cent. A normal factory extract made at 1½ kg. pressure showed:

	Tans	Non-tans	Acids Total	Acids Volatile	Acids Non-vol.	Acids to 100 dry subst. Total	Acids to 100 dry subst. Volatile	Acids to 100 dry subst. Non-vol.
Crude chestnut liquor	4.18	1.73	0.50	0.252	0.248	8.46	4.26	4.20
Same, blood clarified	3.75	1.71	0.43	0.243	0.187	7.87	3.09	4.78
Same, from 1st evaporator	6.40	3.70	0.62	0.336	0.284	6.14	3.33	2.81
Finished extract	28.0	12.80	1.66	0.435	1.225	4.07	1.06	3.01

The acids were computed as acetic. Probably lactic acid is present, derived from blood. The author agrees with Kerr and Wilson that it would be of interest to extract makers to identify the acids accurately, but believes it would often be of advantage to promote the acid formation instead of restraining it. A certain uniformity in acid content is generally reached through action upon the copper of the apparatus, for which reason the author refrains from drawing conclusions from his figures.

W. J. K.

The Wattle Bark Industry in South Africa. *S. African Agricultural J.*, through *Leather Trades' Rev.*, Feb. 19, 1913. The Australian black wattle was first planted in South Africa in 1864. The trees were prized for shade, for wind-breaks, and for firewood before the value of the bark as a tanning material was appreciated. About 1893, Sir George Sutton issued a pamphlet entitled "Wattle Bark a Paying Industry," stating that he had sold the bark to a tanner for experimental purposes as long ago as 1884. In 1887 the first shipment of 10 tons was sent to England. The exports in 1911 were 49,407 tons, valued at about $1,400,000. The tree belongs to the natural order *Leguminosae*. The genus is *Acacia*, (represented in the United States by the "honey locust" and others). Many sorts have been tested in S. Africa, and three found which are profitable for tanning purposes; black wattle and green wattle, which are varieties of the same species, *Acacia decurrens*, and the golden wattle, *Acacia pycnantha*. The first two contain about equal percentages of tannin, but the black is said to yield more bark per acre. The green variety is more hardy and may be grown in regions subject to frost. The golden wattle grows only in certain parts of Cape Colony.

The black wattle requires abundant moisture (20 to 40 in. rainfall per year) and a deep, loose soil, as well as careful cultivation. Plantations should be near railways, so that the wood may be disposed of. Five hundred or more trees are planted per acre. The crop may be cut at five years or any later time. Ten years is perhaps a good average. In this case an average return is 5 tons per acre of dry bark and 30 tons of dry wood. Felling is sometimes completed at one operation, and sometimes extended over several years, a fixed proportion of the crop being taken out at each operation, the remaining trees having thus an opportunity to profit by the increased space. Stripping is usually done in the months which are

dry enough to permit outdoor drying, but since the bark is sometimes too dry to peel during the dry months, it is necessary to have drying sheds. One laborer can fell the trees, and strip and hang up the bark at the rate of 1000 lbs. of green bark per day. The time for drying is from one to two weeks. Many growers bundle their bark and sell it without further preparation to dealers who chop or shred it by machinery and ship it in 3-bushel sacks holding about 180 lbs. each. The shredded and bagged bark is worth from $34 to $36.50 per ton at Dalton. Freight to European points amounts to about $7 per ton. The wood is worth for fuel purposes from $1.25 to $5 per ton, heavier sizes which can be used for mine timbering up to twice these prices. After a crop is cut off, another grows from volunteer seedlings. These generally require to be thinned. The cost of land suitable for the growth of wattle is from $5 to $30 per acre, depending on quality and distance from transportation facilities. The prices given for the London market ($38.50 per ton for ground bark), are inconsistent with previous figures. (A sample of black wattle bark recently analyzed gave about 45 per cent. tannin, with under 10 per cent. moisture. Ed.)

The Cultivaton of Sumac in Sicily. *L. T. Rev.*, April 16, 1913. Sicilian sumac, (*Rhus coriaria*), matures satisfactorily only in the extreme south of Europe. The Sicilians designate two varieties, male and female sumac, the former being richer in tannin and commanding therefore a higher price. (It would appear from the description that the plant is like some of our American sumacs in bearing staminate flowers on one plant and pistillate on another. The method of propagation by slips would make it possible to cover whole plantations with male plants. Ed.) When the plants have reached their third year the shoots which come up around them are used to form new plants. Young and vigorous shoots are chosen, having a short strong root. These are planted in December or January from 24 to 28 inches apart, making about 10,000 plants per acre. A crop of leaves is harvested the first year. The best return is usually realized the third year, the best lands yielding up to ¾ of a ton per acre, for which the grower may receive from $22 to $24 per ton. About one-third of the gross receipts are profit, under the most favorable conditions. The Italian government has made persistent efforts to prevent the adulteration of sumac with "lentisco" and other inferior materials. These inlcude the establishment of a government laboratory at Palermo, where at a price equivalent to about $1.50, samples are analyzed for parties interested. The use of tin salts in silk dyeing has cut off an important part of the market for sumac. Formerly the large dyers bought the leaf and extracted it themselves. Now those who continue to use sumac buy the extract from the makers of tanning extracts.

Leather Dyeing. M. C. LAMB. *S. & L. Rep.* March 20, 1913. In Great Britain it is customary to use acid dyes, while continental leather manufacturers use basic dyes almost exclusively. The writer has asked why this is the case, and has been told by the German and French dyers

that the acid dyes do not give good results. The acid dyes are stronger in coloring power than the acid, but those suitable for use in leather are in general more expensive than the corresponding acid colors. The drawback to the use of basic dyes is their tendency to exaggerate defects in the skin. The reason for their use, Mr. L. thinks, is that they are better adapted for the dipping method of dyeing than the others. The grain surface of the skin consists of a thin membrane of great tenacity, called the "glassy layer," which differs, chemically as well as physically, from the fibrous true skin. Basic dyes have much less affinity for this glassy layer than for the true skin, while the affinity of the acid is the same for both. If there are scratches on the skin, exposing the fibrous layer, the basic dye makes this portion darker. The affinity of the basic dyes for tannin is another disadvantage, since any uneveness in the tannage causes a variation in the shade of the dye. Another disadvantage is the greater liability of the basic dyes to "bronze." The chief disadvantage of the acid dyes is that acid must be added to the dye bath. From the point of view of the color produced, the best acid to use is sulphuric, but unless great care is used to remove the last traces of acid by washing and neutralization, the life of the leather is much shortened. In the case of leathers for book-binding, chair seats, etc., where long life is of the first importance, sulphuric acid should never be used. In such cases it may be replaced by formic acid, which produces almost as good colors. Because of their less affinity for the hide-fiber, the acid dyes require more time than basic. For this reason they are not adapted to the dipping process. They are only employed in the paddle-wheel or drum, requiring from 30 to 45 minutes to color the leather fully. In order to get full shades and exhaust the dye-bath as much as possible, the dyeing should be done at a temperature of about 120° F. when acid dyes are used.

The Quality of Leather. Paper by F. A. Coombs, of the Sydney Technical College, at the Australian Science Congress, Melbourne. Those who deal in leather depend more on practical tests than on chemical analysis for their judgment as to the quality of leather. "Feel," color, solidity, pliability, strength of grain, general appearance, etc., are the things on which the "practical man" bases his opinion. Of the many factors which go to determine the quality of leather, none is more important than the quality of the hide or skin from which it is made. European calfskins are better than Australian, because the calves have been better fed. Sole leathers for damp climates should be hard and solid, but those intended for dry climates should not be hard, or they will be liable to crack. A dressing of hard fat is an advantage for dry climate soles, as the leather will then bend without danger of cracking. If sole leather is kept in process only so long as it takes up tannin in chemical combination, the resulting leather is thin, porous, and lacking in solidity. After making this statement, Mr. Coombs asserts that it is desirable that sole leather should contain no water-soluble matter. The "combined tannin" is found

by subtracting from the total the water, water-solubles, ash and hide-substance. The writer criticizes this practice because if any organic material insoluble in water and containing no nitrogen, such as finely ground spent tan, were drummed into the leather, this method would report such a substance as combined tannin. "Bloom," the material deposited in the leather in oak tannage, in thus reported, and the writer thinks that tanners are quite justified in seeking to find materials which can be drummed in and produce the same solidifying effect as actual bloom.

The Problem of the Waste Liquor from Sulphite Pulp Mills. W. O. WALKER, *J. S. C. I.*, April 30, 1913, XXXII, 389-91. There are three different types of waste from the sulphite pulp industry, digester liquor, filter-press water and condenser water. The first is a dark reddish brown liquid of sp. gr. about 1.05, containing total solids from 10 to 12 per cent. Of the dry material about 12 per cent. is ash, chiefly sulphates of calcium and magnesium. The chief constituent of the liquor is an organic sulphur compound containing calcium, probably a calcium and magnesium lignin sulphonate. Other constituents are small quantities of sulphurous acid, free sulphur, pentose and pentosans, a terpene-like substance and free furfurol; and traces of sulphuric acid, of vanillin or a body very similar to it, and of mannose, dextrose and galactose. The organic sulphur compound first mentioned may be precipitated by alcohol. It is a dark gummy mass which becomes brittle by drying. It may also be obtained by salting it out of the concentrated liquor with salt or magnesium sulphate. It is precipitated by concentrated mineral acids and by lead acetate. It is soluble in water and in dilute alcohol, from which it does not crystallize. It yields brominated and chlorinated derivatives, contains methyl groups and an active carbonyl group, and is a strong reducing agent. The sulphur is in the form of a sulphonic group. The substance is no doubt the soluble reaction product from the magnesium and calcium bisulphites on the complex of groups in combination with the cellulose in the ligno-celluloses. These groups are commonly designated as lignin or lignone. They resemble di-ketones or quinones. The lignone complex has more carbon than cellulose, (44 per cent.).

A number of patents have been taken out for the recovery of the sulphur, but these are not satisfactory, since the organically combined sulphur is difficult to reclaim. Destructive distillation gives a low yield of useful materials. The yield of oxalic acid by fusion with caustic potash is also too low for profit. By precipitation with gelatin a substance has been obtained which when dissolved in weak alkali may be used as a size for paper. The sodium salt of lignin-sulphonic acid has been used as a substitute for lactic and tartaric acids in dyeing. The concentrated liquor has been used as an adhesive for making cores in foundries, and in conjunction with slag meal rich in phosphorus has been used as a fertilizer. R. T. Mohan has investigated the tanning properties of the substance, and finds that the addition of lactic acid improves the tanning properties. Re-

moval of the lime makes little difference in the quality of the leather. Removal of the gummy matters destroys the tanning properties entirely. When redissolved the gums will not tan. The concentrated liquor has been used in briquetting coal dust. The high percentage of ash is a disadvantage. It has also been tried as a cattle food. Most of the proposed uses have been abandoned.

Experiments conducted at Queen's University, Kingston, Ont., indicate that the waste liquor, concentrated to one-fourth volume is better than petroleum for surfacing roads. Some progress has been made in the effort to obtain dyes by treating the liquors with aromatic amines. A process for making alcohol from the waste liquor is being carried on in Sweden. Only about two per cent. of the organic material is fermentable by yeast, so that the alcohol process is only a partial solution of the problem of disposal. Mr. Coombs thinks that the most pressing need in further investigation is the extension of our knowledge of the actual structure of the principal organic ingredient of the liquors.

Cellulose in Tanning Extracts. CH. MONNET. *Le Cuir*, May 1, 1913, and *Collegium*, May, 1913, pp. 224-5. At the last Congress of the I. A. L. T. C. at London, it was decided that any chemist discovering in an extract in the course of his analysis the presence of pseudo-tannin ought to mention the fact in his report. Most of the makers of pure tanning extracts applauded this measure, believing it to be in the interest of their industry. The mention in the report of an analysis of the presence of sulphite-cellulose is a very grave accusation against the maker of the extract, and an expert should not express such a judgment without basing it on several tests, and establishing the point beyond doubt.

Before the Congress, Professor Procter had published his reaction for sulphite cellulose, and it was generally supposed that the indications of this test were infallible. Some recent facts go to show that this test may lead to wrong conclusions. Recently a German firm refused a lot of chestnut extract, claiming that it contained cellulose. On the protest of the maker, samples were sent to a number of experts. The following reported that the extract contained sulphite-cellulose: Procter, Paessler, Hundeshagen and Philip, and Hemixem. The following reported the extract pure: Maschke, Thuau, and the Tanning School at Liége. Dr. Allen, being called on for an explanation of these contradictions, said that normal chestnut extracts do not give the Procter-Hirst reaction. The presence of sulphite-cellulose in the extract in question appearing very unlikely, he concluded either that the wood of which the extract was made was abnormal, or that the extraction was done under abnormal conditions. The maker then sent identical samples to Procter and Paessler. The former reported negative result, and the latter positive. The author concludes that the Procter method is not applicable in every case, or that its indications may be differently interpreted. The Procter-Hirst test ought therefore to be verified by means of other reactions. To

this end he asks for the coöperation of the members of the International Association of Leather Trades Chemists. A definite method of procedure in dealing with sulphite-cellulose extracts is much needed, and the suggestion is made that a commission be appointed to study the pure extracts of different regions and compare their results. L. B.

The Installation of Vats for Extraction. ANON. *Le Cuir,* May 1, 1913. Methods of heating leaches, and of conveying liquor from one to another are described, and the advantages and disadvantages of different methods discussed. The writer concludes from practical experiments that it is better to place steam heating coils above rather than below the false bottom of the leach. No injury to the tannin has been observed from this method, and it favors equal distribution of heat through the leach. One method of moving the liquors is to boil the liquor under the false bottom, and permit the pressure of the steam formed to push the liquor up through a pipe centrally placed in the leach. In another method a steam injector is used. Several illustrative diagrams are given. L. B.

Some Notes on Artificial Leathers. RENE MADRU, chief of the Leather Laboratory of Paris. *Le Cuir,* April 15, 1913, and *Collegium,* May, 1913. pages 209 to 213. Leather has many valuable qualities, and that used for any given purpose utilizes one or more of these. For some purposes it may therefore be possible to produce substitutes for leather each of which shall have the particular quality needed for the purpose in question. It is unlikely that any one substitute can be made that will serve many purposes. Artificial leathers fall naturally into four classes: (1) those having as a base a simple fabric (pegamoids), (2) those having several layers of fabric glued together, (3) those made by felting together vegetable or animal fibers, (4) those whose base is a paste made into sheets. The first kind have either a paper base, treated with a gelatinous solution of glycerin, which is treated with formaldehyde after drying, or of cotton fabric covered with a coating of celluloid, acetate of cellulose or other collodion. The coating is rendered flexible by the addition of castor oil. The second kind are made of layers of cotton, linen, jute or other textile, stuck together with an adhesive which resists the action of water. The third class uses either vegetable or animal fibers. The vegetable fibers employed include ramie, Japanese mulberry, jute, hemp and cotton. These fibers may be employed in the natural state, or treated before being felted together with alkaline solutions, oils, bichromate of potash, etc. They are made into a compact mass by means of rubber, albumen, glue or glycerine. The animal fibers used are obtained from intestines, tendons, etc., which are dried, shredded, felted, swollen by acid or alkaline solutions, and then impregnated with a solution of a gum or with an oxidized resinous oil. The fourth sort of artificial leather is generally made from leather scrap, which is pulverized, treated with acid solutions or lyes, mixed with a binder and rolled or moulded into sheets. The binders which are used include dextrin, soda soaps treated

with sulphate of zinc, albumen precipitated with tannin, boiled oil, and viscose. The author has produced an artificial leather from leather scrap by macerating the scrap for several days in cold water, then in water at 100° F. which is renewed until it ceases to wash out any color. They are then treated with successive baths of carbonate of soda, and finally with an alkaline solution of pancreatin. The fibers are now quite separate and can be made readily into a felt. If the felt is saturated with an albuminous solution and then tanned, a material resembling leather results. The author gives suggestions on the analysis of artificial leathers, pointing out how various substances which might be present may be recognized.

L. B.

Some Notes on the Analysis of Chrome Leather. U. J. THUAU. *Collegium,* May, 1913, pages 206-209; also *Le Cuir,* May 1, 1913. The leather is pulverized, and extracted with petroleum ether for at least 4 hours. After drying, it is extracted with 90 per cent. alcohol for 3 to 4 hours. The leather is now extracted with water in the same manner as vegetable tanned leather. The ether extractive contains the non-saponified fats and any free sulphur. The mixture may be separated by treatment with sulphuric ether which dissolves the fats and leaves the sulphur. Unsaponifiable is determined on the fat in the usual way. The nitrogen is determined as in bark leather. A much used method for the determination of chrome and alumina consists in fusing in a platinum crucible the ash from 5 or 6 grams of leather with a mixture of 4 g. Na_2CO_3 and 2 g. KnO_3, or with 2 g. Na_2CO_3, 0.75 g. KOH and 1.5 g. $KClO_3$, for 25 or 30 minutes. The chrome and alumina are converted into sodium chromate and aluminate. The fusion is dissolved in boiling water, filtered into a 250 cc. flask and made up to the mark. One hundred cc. are set aside for volumetric determination of chrome, and the rest is acidulated, reduced with alcohol and the Cr and Al precipitated with NH_3 and weighed together. The chrome in the 100 cc. is titrated with thiosulphate in the presence of KI in acid solution. Another method, which the author prefers, heats the ash with Na_2CO_3 alone in a muffle furnace for 5 hours. insuring the conversion of all the chrome and alumina into chromate and aluminate. The fusion is dissolved, filtered and treated with hot NH_4NO_3 in excess. The carbonate of soda is converted into nitrate, the chromate remains in solution and the alumina is precipitated completely on boiling the solution to remove excess of NH_3. The filtrate from the alumina is acidulated with HNO_3 and the chrome reduced with alcohol, precipitated as hydroxide and weighed as Cr_2O_3. If NH_4Cl is used instead of NH_4NO_3 or if the carbonate is decomposed with a strong acid and the alumina precipitated with NH_3, some chrome is always carried down. The separation of Al and Cr is becoming more important, as there is a growing use of chrome for a fore-tannage in the case of alum-tanned leather, and some makers give a light chrome tannage at the end to alum-tanned leathers to create the impression that they are entirely tanned with chrome.

L. B.

Mallet Bark. *Bourse aux Cuirs de Liége,* May 4, 1913. This bark has been in the Belgian market for 8 or 9 years. It is sold in small pieces, the interior of which resembles dry extract. Only the flesh is used, the ross being scaly and of little value. The color is lighter or darker, depending on its dryness. Sometimes it grows darker with age, especially when it has been shipped damp. It is the bark of the *Eucalyptus occidentalis,* a tree which grows in Australia, reaching a height of from 65 to 80 feet. The tannin of mallet bark is easily soluble, cold water dissolving 95 per cent. of it. The temperature of extraction should not exceed 60 or 70° C. (140 to 158° F.). The bark may be extracted down to 3 or 4 per cent. Analysis shows tannin 38 per cent., non-tans 11 per cent., water 14.5 per cent. The non-tans include 1.4 per cent. grape sugar and 0.8 per cent. cane sugar. Very strong liquors may be made from mallet bark without much material of low solubility, as is the case with quebracho. Even when exposed to the air, the liquor does not undergo change. The color of the leather is good, resembling that from oak bark, but it has a tendency to darken under the influence of light. Mallet bark has no injurious influence on the leather. Its price is moderate.

L. B.

New Method for the Titration of Sulphurous Acid also together with Thiosulphates. E. BOSSHARD and W. GROB. *Chem.-Ztg.* [37], 465-6. Sod. bisulphite, $HNaSO_3$, is neutral to methyl orange but $NaSO_3$ is alkaline while with phenolphtal. indicator neutrality is not reached until all the $HNaSO_3$ has been converted into Na_2SO_3. The authors have found that this last titration may be made using methyl orange as an indicator if $HgCl_2$ be present which frees the SO_2. In a trial analysis, 10.071 gms. sod. bisulphite were made up to 1 liter, 1 gm. NaCl added to annul the weak acid reaction of the $HgCl_2$ and 50 cc. portions were then titrated with N/5 NaOH: (1) with $HgCl_2$, methyl orange; 21.51, 21.45, 21.55 cc.; (2) without $HgCl_2$, phenol-phtal.; 21.27, 21.27, 21.23 cc. Since with phenolphtal. the change from colorless to red is quite gradual, this new method with methyl orange is easier, simpler and more accurate.

In the titration of mixtures of sulphite and bisulphite, HCl and methyl orange are titrated to orange, neutrality being reached according to the equation $Na_2SO_3+HCl=NaHSO_3+NaCl$, all the sulphite being converted into bisulphite. Next 300 cc. sat. $HgCl_2$ sol. and a little pure NaCl are added, the liquid becoming red. The titration is finished with alkali to disappearance of the red and measures the total SO_2: $HNaSO_3+NaOH=Na_2SO_3+H_2O$. By subtraction of the equivalent of the HCl used to titrate the sulphite, the original bisulphite content is determined.

Thiosulphate is neutral to methyl orange but if excess of $HgCl_2$ sol. be added, HCl is set free and can be titrated (Feld's method): $Na_2S_2O_3+2HgCl_2+H_2O=2HCl+Na_2SO_4+S+Hg_2Cl_2$. The author's method for including sulphites and bisulphites is as follows: (1) Sulphite is first deter-

mined by titrating with HCl, methyl orange indicator. (2) Phenol-phtal. is added and the total SO_2 titrated with alkali to red, the difference between (2) and (1) giving bisulphite. (3) To determine thiosulphate, excess of $HgCl_2$ is added to another sample with 1 gm. NaCl and the HCl formed titrated (methyl orange), first adding 30 cc. 4N.NH_4Cl to avoid precipitation of HgO. The SO_2 present is also included in the titration since $HgCl_2$ is present and must be deducted. Check analysis:

50 cc. $HNaSO_3$ sol. mixed with 9.88 cc. N/10 $Na_2S_2O_3$ (standardized by iodine) required 22.28 cc. N/5 NaOH; deducting 12.45 cc., the amount required by the bisulphite alone (in a separate test), 9.83 cc. for the thio. are left. The acidimetric determination of thiosulphate agrees therefore with the iodometric. W. J. K.

Contributions to the Knowledge of the Tannin of Myrobalans. JOH. PAESSLER and WERNER HOFFMANN. *Ledertechn. Rundschau,* 1913 [5], 129-134.

I. *The Nature of Myrobalans "Bloom."*—For the preparation of material for research, Nierenstein's method of boiling the tannin sol. with dilute H_2SO_4 appears to the authors too severe a treatment for sensitive tanstuffs and they prefer to allow the "bloom" to separate spontaneously from dilute solutions containing 0.5 gm. tans to 100 cc. These are filtered directly after preparation, and left standing protected from air. Dividivi gave small amounts of a thick, brown ppt. only after 4-5 days, but valonia and myrobalans gave large amounts of a light yellow ppt. in a short time. The valonia bloom was identified as very pure ellagic acid; the product from divi-divi also consisted mainly of ellagic acid but in a form difficult to purify. Unlike these two, the bloom from myrobalans was crystalline in character and yielded pure chebulinic acid, a substance first isolated by Fridolin, studied later by Adolphi and recently by Thoms and Richter. These last two investigators found the active ingredient of a pharmaceutical product "Eutannin," made by Vogtenberger & Föhr, Feuerbach, to be chebulinic acid, $C_{28}H_{22}O_{19}$ or $C_{28}H_{24}O_{19}$ of which they studied the properties. On heating with water it forms a hydrate which with acid or alkali splits into 2 mols. gallic acid and 1 mol. of a tannic acid $C_{14}H_{10}O_{12}$.

The present authors recommend their process as suited for the convenient preparation of the above named acid. Portions of finely ground seeded myrobalans summing to 120 gms. are extracted with 8 liters cold water in a Koch apparatus. The extract is filtered immediately through a candle filter and let stand in flasks plugged with cotton. After 5-6 days, the yellow ppt. is filtered off, washed with a little cold water, then extracted with warm (50-60°) 60 per cent. alcohol until filtrate is colorless. On the filter is left a brown, slimy mass from which ellagic acid $C_{14}H_6O_8$ may be extracted by pyridin. This is identified by the Griessmeyer reaction on treatment with a few drops of conc. HNO_3, then diluting, when a fugi-

tive red color develops. A further confirmation for ellagic acid was obtained by combustion analysis of the tetra-acetyl derivative. To obtain chebulinic acid, the alcoholic extract is concentrated in a vacuum and then poured into water. After standing, the separated crystals are re-crystallized from warm water washed with ether to remove traces of gallic acid and then dried in vacuo over H_2SO_4. The compound then contains 1 mol. H_2O of crystallization which goes off at 100°; it decomposes without melting at 225-7° (Thoms, 234°). The combustion gave:

			$C_{28}H_{24}O_{19}$ computed	$C_{28}H_{22}O_{19}$ computed
C =	50.73	50.82	50.62	50.74
H =	3.34	3.38	3.62	3.35

The specific optical rotation was found to be $[\alpha]_D = 64.41°$ for a 3 per cent. aqueous alcoholic solution after standing 30 hours. Adolphi and Thoms found 61-67° for the crystallized compound in absolute alcohol sol. during 6 days; and Richter found a constant of 58.9° for the anhydrous substance in absolute alcohol. Water therefore seems to affect the rotation, equilibrium being reached with large amounts. Of the principal reactions of chebulinic acid are mentioned: solubility in alkalies with yellow color changing to reddish yellow; blue sol. with $FeCl_3$, becoming flocky on heating; lime water, yellow ppt.; ammon. Ag. sol. reduced in the cold, Fehling's sol. on boiling; gelatine pptd. by hot H_2O or alc. solution. An individual reaction is an olive green color with ammon. vanadate which after addition of a little H_2SO_4 and warming gives a permanent decided grass green. The soluble hydrate was made according to Thom's directions by boiling with water under pressure. The product yielded 97 per cent. tans (filter method). To obtain larger amounts of chebulinic acid, 20 gms. of "Eutannin" were heated with 300 cc. of H_2O in an autoclave at 100°, yielding a clear sol. of 2.8° B., giving 79 per cent. tans (shake) rated on total solids = 100. This liquor yielded with calf grain split a thin, hard leather, rendered brittle doubtless by gallic acid which was evident in all the filtrates from hide. The sole (but expensive) advantage of chebulinic acid for the tanner is the bright color imparted to the leather by the bloom. The authors believe the acid to be present in the fruit as a glucoside and as such to go into solution and later this is split by hydrolysis or a ferment derived from the fruit. If such a solution be heated, the soluble hydrate is formed and no separation ensues. The best yield obtained from various stocks of myrobalans was 3-4 per cent. chebulinic acid.

II. *Alterations in Myrobalans Liquors.*—Several investigators have studied the loss of tannin. Eitner (*Gerber* (1892) 245, (1893) 1) found the loss on treatment with oxygen was due to fermentation and that it was negligible on sterilization. Youle and Griffith (*J. S. C. I.* (1901) 428) found that fairly strong liquors of 8-13° B. lost progressively 13.6-22.2 per cent. of total tans in 11-188 days. Paessler and others found similar, losses with dilute liquors, but little change in the commercial

concentrated extracts (25° B.). The authors have here repeated the above investigations with a view to the best utilization of the tannin.

Exp. I.—To test the effect of sterilization, a solution of analysis strength containing 70.0 per cent. total solubles (myrobalans = 100) 49.1 tans (shake) was divided and let stand, one portion being first sterilized by repeated heating to 70-80°. After 10 days the analysis gave: sterilized total solubles 68.2, tans 45.6; unsterilized, total solubles 57.4, tans 37.4. The sterilized liquors remained clear with little change while the unsterilized contained much sediment. This was not due to bacterial action, for disinfectants (phenol, boric acid, SO_2, etc.) did not hinder the separation neither was a pptn. induced in the sterilized liquor by inoculation from the other. Nor did oxygen appear to produce the result. The peculiar behavior of myrobalans liquor is attributed to the presence of chebulinic acid which with hot water splits up into soluble components. This is probably the cause of the permanence of boiled liquors.

Exp. II.—A series of liquors were warmed ½ hour at varying temperatures 30-75° and let stand. It was found that at 45° there was considerable reduction in sedimentation and at 50-60° this was very marked.

Exp. III.—Analyses were made in this series. A liquor of 68.2 total solids, 42.8 tans, gave 56.5 and 37.0 after standing 12 days. A parallel test previously warmed ½ hour to 45-55° gave 57.9 and 35.6, showing the action to be slight at this temperature; 70-80° is more effective.

Exp. IV.—Various methods of leaching were tried, 12 gms. to the liter. After 12 days the loss in tans (total tans = 100) was with cold leaching, 23.8 per cent.; leaching at 50°, 18.8; at 100°, 8.3; 2 hours at 1 atmosphere over pressure, then cold leaching, 15.6; same, 2 atm. 3.3; same, 4 atm. 5.8; same 6 atm. 4.4; 5 hours heating dry at 40-50, then leached at 50°, 22.0; same leached at 90°, 6.0; treated 1 day with SO_2, then leached hot, 14.3; leached at 90°, liquor then boiled hard ½ hour, 3.2 per cent. The pressure extraction reduced the loss but is impractical because the liquors become dark colored and do not filter clear and there is considerable loss of tannin (1st day, analysis 27.3 tans, 6 atmospheres extraction, compared with 42.2 tans, cold extraction). The best results were obtained by boiling the liquor as Procter and Parker have already shown; they also found 90° a favorable leaching temperature, which was confirmed by the author's observations. The liquors thus obtained should be kept ½ hour at the same temperature which would ensue of itself in a large battery.

Exp. V.—Solutions (analysis strength) of four commercial myrobalans extracts were examined after 12 days; the losses were from 5.7 to 11.4 per cent. of the total tannin. W. J. K.

Review of Analysis and Chemistry of Fats for 1912. W. FAHRION. *Zeit. angew. Chem.* 1913 [26], 181-197.

Fat Extraction.—Huggenberg's burette has been improved. Cl. Grimme

(*Chem. Rev.* [19] 1) finds that Neumann's shake method (ante, p. 58) without a Soxhlet extractor can be used universally with trichlorethylene or carbon tetrachloride, all other solvents being unsuited; ½ hour shaking suffices which Neumann (*Chem. Ztg.* [36] 150) disputes.

Physical Constants.—R. Pronzergue (*Chem. Zentralbl.* I, 1150) uses an original device for determining melting points. At the moment of melting contact takes place between a dilute lye and phenolphtal. solution, giving the red reaction. *Total fats, Free Acids.*—Lenk and Mondschein (*Chem. Ztg.* [36], 534) recommend caution in the employment of phenolphtal. as indicator in presence of alcohol and sal ammoniac, which may give too high acid numbers. M. Hübener (*Chem. Zentralbl.* I, 1634) adds xylol to the alcoholic lye to secure complete saponification in ¼ to ½ hour. *Separations.*—R. Beer (*Chem. Ztg.* [36] 364) recommends Farnsteiner's method for separation of solid from liquid fat acids and Hertz's method for separating the individual solid acids, replacing magnes. acetate by lithium acetate. According to Facchini and Dorta (*Chem. Rev.* [19] 77) liquid and solid fat acids may be separated at least as completely as in Varrentrapp's method, by treatment of the potash salts with 90-95 per cent. acetone. The salts of the unsaturated acids are completely soluble while those of the fatty acids dissolve only in hot acetone and crystallize out on cooling. *Unsaturated Acids.*—Auguet (*Chem. Zeit. Rep.* [36] 672) adds hydriodic acid to the Hübl solution to make it more stable. The reporter (Fahrion) disputes his assertion that one hour's action of the Hübl sol. suffices. According to C. Stiepel, Marcusson and Huber's method (abstr. this JOURNAL [7] 181) for detection of fish oils fails with chemically altered oils. On heating these the hexabromide number falls rapidly. Eibner and Muggenthaler have made a study of the conditions affecting the formation of hexabromlinolenic acid. Pure ether is the best solvent and it is not desirable to brominate the oils directly, the ppts. filtering with difficulty. In brominating the fatty acids, the hexabromide number is affected by the concentration of the lye used in saponification, also by the amount of solvent ether, a 10 per cent. solution being best. The pure hexabromide melts sharply at 177° (confirming Fahrion). They found the number higher than previously published and specify accurately the details which the author regards as too complicated for practical work. *Unsaponifiable.*—A. Windaus (*Ber.* [45] 2421) has arrived at a constitutional formula for cholesterin. F. F. Knorr in determination of unsaponifiable shakes the petrol. ether solution with water containing a "few drops" alcohol. (The reporter maintains that this does not fully remove traces of soap dissolved in the petrol. ether because of dissociation by water and solution of the freed acid by the petrol. ether; 50 per cent. alcohol must be used.)

Constants of Linseed Oil.—Wolff and Meister point out that pure oil may sometimes have an iodine number below the limit 170. Nigemann and Kayser found for various oils: North Russian 190.1, South Russian, 171.7, Indian 183.8, Argentine 179.3; Baltic oil, giving the highest number,

is known to give the best varnish. This oil has the highest refractive index and this constant is held to be a direct function of the iodine number and the double unions. Eibner and Muggenthaler found that the Baltic oils also gave the highest hexabromide numbers (Baltic 57.96, Dutch 51.73, Argentine 51.66, Indian 50.5).

Fat Reduction (Hardening, Hydridizing).—One of the most important problems in fat technology at the present time is the conversion of liquid oleic acid $C_{18}H_{34}O_2$ into the solid stearic acid $C_{18}H_{36}O_2$. This is now solved and fish oils form the cheapest raw material. The stearine produced (Talgol, Candelite) is used in the soap industry. Many patents have been taken out for the process, all involving the addition of free hydrogen in the presence of various catalyzing agents such as metals, oxides and salts of organic acids. The stearine thus produced (although odorless) is considered inferior to the natural article and its economy is at present in question. "Hardened" oils have not yet been introduced in food fats but enterprises are under way in this direction.

Fat Hydrolysis.—Vandevelde and Vanderstricht (*Chem. Zentralbl.* II, 1572) have experimented in fractional saponification using excess of fat. With swine fat the saponification numbers of the saponified and unsaponified fats were found about equal while with butter and cocoanut oil the number was lower with the unsaponified component showing that the acids of lowest molecular weight were first attacked. *Stearin.*—H. Dubovitz finds that with 100-200 gms. of fat acids, it is possible to apply the technical process of cold and warm pressing for a quantitative determination of the stearin and olein. W. J. K.

Researches on Bran and Straw Bates. Dr. Hugo Kuhl. *Ledertechn. Rundschau* [1913], 1-2. Assays of 300 gms. of rye bran were let stand in flasks with varying amounts of water and 40 cc. of the resulting products titrated with ¼ N standard alkali. The first lot with 3 parts water required 18.5, 1.0 and 0.5 cc. alkali after standing 5, 10 and 14 days respectively; another similar test required 6, 72 and 0.25 cc. When 10 parts of water were used, 11.2, 12.8 and 11.2 cc. alkali were required after 5, 10 and 12 days; another test used 12.4, 18.5 and 14.5 cc. A test with 30 gms. oat straw and 5 liters water consumed 1 cc. alkali after 5 days and 0.5 cc. in 12 days; this agrees with tannery experience, this being a milder bate. W. J. K.

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CORRECTIONS.

Page 232, twelfth line from bottom, "Herbert W. Griffith" should be Robert W. Griffith.

Page 262, first line, "The acid dyes are stronger" should read, The basic dyes are stronger.

THE TANNING PROPERTIES OF LOGWOOD.

By Roy H. Wisdom.

Logwood, according to Procter, contains about 3 per cent. of tannin. He also states that its coloring matter is haematoxylin, a substance nearly allied to tannins.

Analyzed according to the official method of the American Leather Chemists Association, a fairly representative sample gave the following results:

	Per cent.
Moisture in wood	17.33
Total solids	15.23
Soluble solids	13.65
Insolubles	1.58
Non-tannins	5.83
Tannin	7.82

Of course, the general term logwood is rather broad, for we know that the tinctorial value varies considerably with the source, and this variation would in all probability hold good as regards the tannin content as well. But such a wide discrepancy is rather disconcerting and if Professor Procter's statement is true, we are again up against the old question of what constitutes tannin. It is possible that the haematoxylin which he states as being nearly allied to tannins, has considerable bearing on the matter. However, if we are to accept the findings of the official method of the American Leather Chemists Association, we must give logwood a somewhat higher tannin rating than has heretofore been accorded it.

A pure clarified logwood extract analysed in this laboratory gave the following results:

	Per cent.
Total solids	44.83
Soluble solids	44.69
Insolubles	0.14
Non-tannins	20.79
Tannin	23.90

With the exception of the insolubles, this is not unlike the analysis of an oak bark extract. Therefore we can reasonably expect such an extract to be capable of making leather. That such is the case can be attested, for the writer has made an excellent quality of leather from this extract.

In view of the above, it may be of interest to the tanner who uses vegetable tanned leather as a base for his logwood colors, to look into the matter of using a certain proportion of logwood with his other tanning materials in the tan-yard, as it would mean that when he reached the dyeing stage, the logwood being already combined with the leather, his process would be just that much shortened and he would be assured of a more uniform and even dyeing. Of course, the writer realizes that the high cost per unit of tan would be a considerable factor, but its advantages would seem to hold out possibilities. The writer has had considerable success in producing blacks on leather in which logwood has formed 20 per cent. of the vegetable tanning agent.

In conclusion, the mere fact that logwood alone will produce a full, firm leather should convince any tanner who is now or contemplates using logwood for colors, that it cannot be otherwise than beneficial to his leather both as to weight and quality.

LEATHER INVESTIGATIONS: THE COMPOSITION OF SOME SOLE LEATHERS.*

By F. P. Veitch and J. S. Rogers.

Vegetable-tanned leather is essentially a compound or mixture of hide or fibrous proteid material with tannin. Depending on the use to which it is to be put, it may be finished in several ways whereby the composition of the final product may differ greatly from the simple compound. The tanned leather may be used without material change in composition, as for shoe

* Bulletin of the Department of Agriculture, Bureau of Chemistry.

soles; it may be greased, as for harness and belting; or it may be greased and dyed, as for harness and shoe uppers.

In addition to the insoluble hide and tannin, which are the essential constituents of leather, moisture, mineral matter, fats, and water-soluble tanning materials, which remain to a small extent in well-scoured leather, are present. All of these, when not present in excessive quantities, are proper and normal constituents of the leather. In fact, the presence of a large percentage of oils or fats, even in sole leather, is of decided advantage in increasing the water resistance, flexibility, softness, and life of the leather, while the presence of a small amount of uncombined tannin is often of some advantage in retarding water penetration and hardening of the leather and in making it solid and firm. The presence of a large excess of uncombined tannin materials other than those mentioned is useless or harmful.

Leather is not a definite compound and is therefore impossible to produce of an exact composition. The ratio of combined tannins to hide substances approximates 7 to 10 (see last column of table on pp. 286 to 290), while the percentages of water-soluble constituents, mineral matter, fat, and moisture may vary considerably. Careful study of the analyses of well-tanned, scoured leathers of various tannages, both American and foreign, warrants the conclusion that well-tanned, merchantable, scoured sole leather of all tannages on analysis should give results on a moisture-free basis which fall between the following limits: Leather substance from 75 to 93 per cent., hide substance from 43 to 57 per cent., combined tannins from 31 to 42 per cent., water-soluble materials from 5 to 15 per cent., oils and fats from 1 to 6 per cent., ash from 0.25 to 1 per cent.

Well-tanned, honestly made leather should approach the upper rather than the lower limits for leather substance and oils and fats. The water-soluble constituents should consist only of the materials contained in the adhering tanning solution which have not been removed in scouring.

Properly air-dried sole leather should not contain, even in very damp weather, more than 20 per cent. of moisture, and the average percentages for the year should fall below 15 per cent. Neither the ultimate buyer nor the shoe manufacturer should be

called upon to pay for a greater average amount than this. It will be observed that the leathers reported herewith contain much less moisture, due largely to the fact that they dried out very much after reaching the laboratory.

Normal vegetable-tanned sole and harness leather when burned should not leave more than 1 per cent. of ash and as a rule not more than 0.5 per cent. This ash is derived from the hide, from the lime used in unhairing, and from the salts usually dissolved in all waters. The magnesia of the ash when calculated to Epsom salts ($MgSO_4+7H_2O$), the form present in air-dried leather, should not exceed 1 per cent.

It is customary abroad to consider less than 2 per cent. of glucose permissible, the assumption being that this amount may be present from the tanning materials. It is very doubtful if this amount of glucose is ever present in normal leathers from which the excess of tanning materials has been properly washed. Leathers on which the final liquors were sweet and exceptionally concentrated, and which are subsequently washed but little, may contain between 1 and 2 per cent. of sugars, determined as dextrose.

The ether extract or fat may be as high as 5 per cent., probably never much less, to give pliability, water resistance and durability to the leather.

Weighting of Leather.

During an extended examination of sole leathers now in progress, it has been found that a surprisingly large percentage contains great quantities of foreign materials. Although it has long been known that some tanners make a practice of weighting or loading their leather, the extent of the practice is not appreciated outside the tanning and closely related industries. Tanners state that leather is loaded with foreign materials because the boot and shoe makers will buy only the lower-priced leather, which, to use a trade expression, "cuts to advantage," that is, from which the greatest number of soles can be cut at the lowest cost a pair. Many boot and shoe manufacturers claim that they use loaded leather because it cuts to better advantage than the same leather not loaded.

The character, value and wearing quality of leather varies with the part of the skin from which it is made. The skin from the upper part of the body and along the back is closer fibered than that from the lower part, under the body; it becomes more open textured and consequently more porous as it passes from the backbone to the under side of the body. The skin over the posterior portion of the body is of closer texture than that over the forequarters; consequently the best leather is made from the hide in the region of the kidneys and hips, provided the skin is sound and not damaged in tanning. The leather from the "flanks" and "bellies" is more porous, lighter and more flexible than that made from the "back," and in cutting the side of leather into soles the lighter and more flabby the lower portions the more of it is rejected. If, however, this lower portion has been stiffened and weighted with foreign material, no matter how useless it is nor how soon it may wash out, some shoe manufacturers will cut it into soles, thus obtaining more soles from a side. Because of these facts the shoe manufacturers calculate that weighted leather costs them less for each pair of soles than the unweighted leather.

Unloaded flabby leather makes poor shoe soles, and loading with materials readily soluble in water, as glucose and Epsom salts, increases the cost to the purchaser, and does not make soles more serviceable.

WEIGHTING MATERIALS AND THEIR EFFECTS.

Loading or weighting materials are cheap. Those in most general use in this country are glucose, selling at 2 cents a pound; Epsom salts, or magnesium sulphate, selling at 1 cent a pound; and solutions of tanning or other organic materials, selling at 0.75 to 2 cents a pound. Barium sulphate and lead sulphate—generally formed by drumming the leather first in a solution of barium chloride, costing 2 cents a pound, or of sugar of lead at 9 cents a pound, and then in sulphuric acid—and sodium sulphate, costing 1 cent a pound, are also employed to a small extent. Of these loading materials, glucose, soluble organic materials containing little or no tannin, magnesium sulphate, barium sulphate, lead sulphate, and sodium sulphate are much

more objectionable than a small excess of actual tanning material.

Loading with glucose, Epsom salts, barium sulphate, lead sulphate, excessive quantities of tanning materials, or with water-soluble organic material is often detrimental to leather. It is made hard, brittle, more likely to crack, and after the loading washes out, as usually happens quite readily except in the case of barium and lead sulphates, it is more easily penetrated by water. Loaded leathers are more expensive, less durable, and a menace to health. A distinction should possibly be made between the effects of an excess of true tannin and of other uncombined or loading materials. The excess of true tannin may not itself be so objectionable and may even be of temporary advantage, because the slowly soluble tannins make the leather more water resistant and impede the removal of combined tannin from the leather.

QUANTITY OF ADDED WEIGHTING MATERIALS.

The amounts of materials found in the loaded leathers examined are summarized as follows: Ash, from 0.2 to 2.7 per cent.; ether extract, from 0.4 to 5.6 per cent.; Epsom salts, from 0.2 to 7.5 per cent.; glucose, from 0.2 to 12.4 per cent.; water-soluble materials, from 13.4 to 34.3 per cent.; water-soluble tannin, from 6.1 to 17.8 per cent.

If it is feasible to secure the lower figures, as it appears to be in a number of tanneries, the higher figures must represent very excessive quantities. A comparison of these, together with those in the table on pages 286 to 290, with the figures given for normal leathers shows that the percentages of ash, Epsom salts, glucose and water-soluble materials are, as a rule, above the permissible quantities, while the amounts of fats and oils and actual leather substance are lower than they should be. These figures show a serious moral, economic and business condition. Approximately 63 per cent. of the leathers examined are weighted with glucose, Epsom salts, or both. This loading varies from 1 to 7.5, with an average of 3 per cent. of Epsom salts, and up to 10.4, with an average of 5.5 per cent. of glucose, and amounts to a total maximum loading, when both are present, of 16 per cent. and an average of 8 per cent.

WASTE OF MATERIALS IN WEIGHTING SOLE LEATHER.

The tanners whose leathers have been examined produce a large percentage of the sole leather made in this country. It seems probable, therefore, that these samples are fairly representative of American sole leather, and if this be true, fully 60 per cent. of the sole leather is loaded with Epsom salts or glucose or both, and practically all of it contains more uncombined tanning materials than it should.

If 60 per cent. of the sole leather contains an average of 8 per cent. of Epsom salts and glucose, at least 150,000,000 pounds have been weighted annually with no improvement in its wearing value. The people have paid for not less than 12,000,000 pounds of Epsom salts and glucose, plus a profit to the tanner for working them into the leather, and have obtained nothing of value thereby. The average amount of water-soluble material in these sole leathers is 23 per cent. Subtracting from this the average percentage of glucose and Epsom salts found gives the percentage of what for brevity may be called "uncombined tanning" materials, meaning the materials derived from the tanning liquors in which the leather was tanned.

The almost universal practice of weighting or loading with excessive quantities of uncombined tanning materials is perhaps the most reprehensible form of weighting. It is needless and wastes valuable materials which can be employed in the production of more leather, and it often leads to bleaching or addition of glucose or Epsom salts to conceal the injury which frequently results from the presence of excessive quantities of uncombined tanning materials. The elimination of this waste would not only conserve our fast-diminishing native tanning materials, but reduce the quantity imported, and thus help maintain the balance of trade in favor of this country. It is an astonishing fact that practically all the leathers analyzed contain as much uncombined tannin as good quality oak or hemlock bark and many contain much more. Inspection of the tables shows that approximately one-third of the tannin in these leathers is uncombined, the quantity varying from 9 to 17 per cent. This is sufficient to tan one-third as much sole leather as is now made. Fully half of this wasted tannin can and should be saved. It is

worth approximately $1,000,000 and would tan approximately 100,000,000 pounds of leather. This tanning material is now practically a total loss.

For the past 15 or 20 years energetic efforts have been made to prepare from the waste liquors produced by making paper from wood by the sulphite process products that will tan hides. The woods from which paper pulp is made, with but few exceptions, do not contain more than from 2 to 4 per cent. of tannin. If this is all removed by the sulphite liquors which are subsequently concentrated to 50 per cent. solids, the concentrated material offered for tanning purposes can contain at most but 4 or 5 per cent. of tannin. Up to the present efforts to make leather with waste sulphite liquors have been crowned, at most, with but indifferent success, and in no case do the makers of these products from sulphite liquors advocate that they be used alone in tanning, but always in mixture with materials of known tanning value. These materials are now receiving careful attention from several sources for determining finally whether they have a proper place in the making of leather. Until such time as it shall have been shown that these products will make serviceable leather or that they contribute to the desirable qualities of leather they should not be used in commercial tanning.

DETECTION OF WEIGHTING.

Although it is not practicable for the ordinary individual to determine whether the leather in shoes has been weighted or loaded, the shoe manufacturer can do so in a very simple way. Large quantities of Epsom salts give leather the characteristic bitter taste of the salts, while glucose in quantity gives the leather a very faint sweetish taste.

Whether or not leather has been loaded with soluble materials can be readily determined by anyone by the following simple procedure: Grind a sample of the leather (a pair of soles serves well) to a coarse powder in any convenient way. The leather may be rasped, cut with a chisel or shears, ground in a mill, or sawed. Weigh 100 grams of the ground leather on a scale that will weigh accurately to 1 gram. Place it in a small, dry, close-textured cotton bag which has been washed to remove the starch

and other dressing materials from the fabric and which has been given an identifying mark which will not wash out in hot water. Tie securely the mouth of the bag, weigh the bag and leather carefully and record the weight. Place it in running water as hot as can be readily borne by the hand, and wash out the soluble materials by thorough kneading for 15 minutes. Squeeze out the water and dry over the radiator or in any convenient way until the leather is perfectly dry. Cool and weigh again. The loss in weight represents the amount of soluble matter which has been washed out. This loss in grams, as thus determined directly represents also the percentage loss, and if this exceeds 15 per cent. the leather may safely be said to be weighted.

The following figures show some results actually obtained by this method and also the results obtained in careful analysis of the leather:

WATER-SOLUBLE MATERIAL IN LEATHER.

	Water-soluble material		
Sample No.	Regular analysis per cent.	Washed out in 10 minutes per cent.	Washed out in 20 minutes per cent.
2119	25	20	20
2127	28	24	24
2130	32	34	34
2134	25	24	24

For practical purposes the results obtained in this way are sufficiently accurate.

Bleaching of Sole Leather.

Leather which has been properly tanned with liquors made from chestnut or rock oak bark has been considered for generations to be the best for shoe soles. This leather has a bright light-oak color, the price which it brings depending very largely on this brightness and uniformity of color. As it comes from the tanning liquors leather is often quite irregular in coloring, and when made from nearly all other vegetable tanning materials it is darker in color than that tanned with oak bark. Irregularity of color is not necessarily a sign of inferiority, but, as a matter of fact, it generally indicates damage done in the preparation, tanning, or finishing of the leather, or stained or damaged places on the original hides. The shoe manufacturer knowing that uni-

form color is characteristic of hides properly prepared, tanned and finished, and that oak bark makes a bright-colored leather, demands light, uniformly colored sole leather. The wearer of shoes also prefers leather with a good, clear, even color.

To secure the higher price which this much-desired uniformity, brightness of color, and the appearance of oak-tanned leather brings, the leather is bleached. Solutions of soda and sulphuric acid applied successively, oxalic acid, or oxalic acid and tin chlorid are the chemicals with which this is usually done. The treatment removes some of the excess tanning material from the surface and gives the leather a much lighter color. Bleaching is especially detrimental, as the sulphuric acid is rarely completely neutralized and consequently greatly hastens the rotting of the leather. The cost of the leather is increased by this procedure; the serviceability of the leather is decreased, and the superior appearance secured in this way permits the fraudulent sale of the leather at a higher price. The bleaching of heavy leather is the most useless and harmful of all leather-making practices, and the most vigorous efforts should be made to eliminate it.

Misbranding of Leather.

Formerly all sole leather made in this country was tanned with oak or hemlock bark or a mixture of the two, and the leather so tanned was known as oak, hemlock, and union (oak and hemlock), respectively. More leather is tanned now with quebracho than with oak, and more with quebracho, mangrove, myrobalan, gambier and chestnut, collectively, than with hemlock. Nearly half of the vegetable-tanned leather made in this country is tanned with materials other than oak and hemlock bark. Nevertheless, practically all vegetable-tanned leathers are still termed oak, hemlock or union.

The figures in the table (pp. 286 to 290) show that many of the leathers are misbranded as to tannage. The tannin-free water extract from a leather tanned with chestnut oak is fluorescent when made faintly alkaline. It will be seen that the water solubles from some of the so-called oak leathers are not fluorescent; these leathers were not tanned with chestnut oak. The figures for water-soluble materials also show that many of these

leathers were tanned with tanning materials other than oak or hemlock bark. Tanning liquors made from nearly all materials now used in this country, such as oak, hemlock, and mangrove barks, chestnut and gambier extracts, and myrobalan, contain approximately 2 parts of tannin to 1 part of non-tannin, not including in the non-tannin the sugars which the materials contain, which are fermented to acids and do not, therefore, add directly to the weight of the leather. Quebracho extract, on the other hand, contains approximately 7 parts of tannin to 1 part of non-tannin.

In the last stages of tanning, the leather is in contact with practically fresh normal liquors in which the relations just stated hold. Therefore the tannins and non-tannins of the water-soluble extracts from leather will tend to approximate the same ratio to each other as the liquors in which it was tanned. If the sum of glucose and magnesium sulphate is subtracted from the figures for the non-tannins in any particular leather, the difference approximates the non-tannin figures for the liquor in which the final tanning of the leather was coducted. A comparison of this figure with the figures for soluble tannin shows the ratio of tannin to non-tannin in the liquor, and in many instances proves conclusively that tanning materials other than oak or hemlock bark were used. In fact, the ratio indicates that quebracho was used, but no intimation of the fact is given in the branding of the leather. The branding of all leathers—"oak,," "hemlock," or "union"—is deceptive and the practice should be discontinued. No leather should be branded oak, hemlock or union which is not tanned entirely with oak or hemlock or a mixture of the two.

The misbranding of leather is indicated by the recent census statistics. The percentage of oak leather reported in 1909 is 7 per cent. greater than in 1904; the percentage of union leather is 32 per cent. greater in 1909 than in 1904; while the quantity of hemlock and oak barks and extracts used in 1909 is materially less than in 1904.

Prevention of Weighting and Bleaching.

It is improbable that the present practices of weighting and bleaching sole leather will be voluntarily discontinued by the

tanner. Intelligent buying on the part of the public will do much to break up these practices. The individual purchaser, of course, can not know whether the leather in the shoes he buys is weighted or has been bleached, but if he will insist that they shall not be made of weighted or bleached leather and will not buy from those manufacturers who make such leather, the quantity of leather so treated will materially decrease, and it will be found that shoes are more durable and consequently less expensive.

The weighting and bleaching of leather may be easily and absolutely controlled by concerted action on the part of the shoe manufacturers. It is very simple for them to determine whether the sole leather delivered is weighted, and if they will refuse to buy such leather it will not be made. Shoe manufacturers will see to it that sole leather is not weighted if the public will take sufficient interest in the matter to demand unweighted leather.

Results of Analysis.

In the following list are given the names of the known tanners of the samples examined. These tanning firms are among the most representative producers of sole leather in this country. Probably a number of the leathers, the source of which is not known, were tanned by these known firms, but there is reason to think that many of them were produced by other tanners of sole leather.

MANUFACTURERS OF LEATHER.

Allen, N. R., & Sons, Kenosha, Wis.
American Oak Leather Co., Cincinnati, Ohio.
Cover & Co., Philadelphia, Pa.
Deford, The, Co., Baltimore, Md.
England-Walton Co., Philadelphia, Pa.
Harrington, Frederic, Dunnellen, N. Y.
Howes Bros., Boston, Mass.
Janney & Borrough, Philadelphia, Pa.
Kistler Lesh Co, Boston, Mass.
Leas & McVitty, Philadelphia, Pa.
McAdoo & Allen, Philadelphia, Pa.
Mooney, W. W., & Sons, Columbus, Ind.
Pfister & Vogel Leather Co., Milwaukee, Wis.
Rippman & Sons, Millerstown, Pa.
Smoot, C. C., & Sons, Alexandria, Va.
Toxaway Tanning Co., Rosman, N. C.
U. S. Leather Co., New York, N. Y.
Vaughau, Geo. C., Salem, Mass.
Vulcano Tanning Co., Boston, Mass.
Wilkinson, Rieger & Jones, Philadelphia, Pa.

The analytical results, so far as they are indicative of weighting or the presence of useless or harmful materials, are given in the following table:

Analysis of Leather

Sample No.	Place sample was obtained	Time sample was obtained	Description of sample	Tannage claimed	Fluorescence	Moisture Per cent.	Ash Per cent.	Petroleum ether extract Per cent.	Water-soluble material: Tannins Per cent.	Water-soluble material: Non-tannins Per cent.	Water-soluble material: Total soluble Per cent.	Epsom salts Per cent.	Glucose Per cent.	Combined tannins Per cent.	Hide substance Per cent.	Ratio of combined tannins to hide substance
513	Boston, Mass.	1906 February	Sole, supposed to be weighted	Oak	+	7.5	0.95	1.5	12.7	14.0	26.7	. . .	5.4	26.1	37.9	0.69
1304	do	1907 February	No. 1, Texas oak sole	do	+	6.9	0.8	4.9	17.0	6.8	23.8	. . .	1.5	24.7	39.4	0.63
1305	do	do	No. 2, Texas oak sole	do		6.5	2.1	1.7	10.2	18.9	29.1	3.9	5.7	30.9	31.5	0.98
1306	do	do	No. 3, Hemlock sole	Hemlock	—	7.3	1.9	2.2	14.8	11.9	26.7	1.5	7.2	25.8	37.7	0.68
1307	do	do	No. 4, Oak sole	Oak		6.9	1.2	4.0	15.1	6.4	21.5	0.5	2.6	29.2	38.1	0.77
1308	do	do	No. 5, English pure bark	. . .	—	7.3	2.3	1.3	14.2	11.3	25.5	0.7	0.7	27.0	38.6	0.70
1309	do	do	No. 6, Hemlock sole	Hemlock		7.7	1.0	1.3	17.7	11.5	29.2	1.2	4.6	24.1	37.4	0.64
1400	Baltimore, Md.	do	Oak sole	Oak		6.8	2.6	1.0	14.9	18.4	33.3	4.7	12.0	21.4	37.2	0.58
1401	do	do	Union sole	Union	—	8.3	2.7	2.5	13.2	14.8	28.0	6.4	6.1	27.5	33.4	0.82
1402	do	do	Texas oak sole	Oak		8.3	1.7	1.5	13.7	13.1	26.8	4.0	5.3	28.5	34.6	0.82
1403	do	do	Hemlock sole	Hemlock	—	6.3	1.8	0.4	7.5	19.2	26.7	4.6	10.0	29.5	36.8	0.80
1404	do	do	Texas scoured oak	Oak		7.3	0.7	2.0	14.8	7.1	21.9	0.4	2.3	28.0	40.5	0.69
1405	Boston, Mass.	do	Drum tanned	. . .	—	7.6	0.9	0.7	13.4	2.9	16.3	1.2	0.0	26.1	49.0	0.53
1406	do	do	do	. . .	—	7.9	0.9	1.0	10.2	3.2	13.4	0.4	0.2	27.5	49.9	0.55
2077	Unknown	June	No. 1 sole, No. 2 bend	Union	—	8.8	1.9	3.2	14.4	16.1	30.5	4.4	9.2	23.8	33.4	0.71
2078	Alexandria, Va.	do	Scoured oak sole, No. 1 bend	Oak	—	4.4	0.3	4.7	15.6	4.6	20.2	. . .	1.2	33.0	37.4	0.88
2079	do	do	do	do		3.6	0.2	3.3	14.9	5.1	20.0	. . .	1.8	32.5	40.3	0.81
2080	do	do	Scoured oak, extract tanned (in wheel after vat)	do	—	3.8	0.3	3.5	14.2	5.0	19.2	. . .	1.5	33.3	39.9	0.83
2081	do	do	Vat-tanned belting, No. 1 butt	. . .	—	4.9	0.2	5.3	11.5	5.5	17.0	. . .	1.3	34.5	38.0	0.91
2082	do	do	No. 2 side	Hemlock	—	5.8	0.9	3.3	14.8	12.1	26.9	1.4	6.2	28.0	35.7	0.78
2083	do	do	Oak	Union		5.9	1.2	4.5	14.2	9.7	23.9	2.4	2.7	30.8	34.6	0.89
2084	Washington, D. C.	do	Scoured oak	Oak		6.3	1.0	5.5	13.6	10.8	24.4	3.0	2.5	27.7	35.8	0.77
2085	do	do	do	do		7.0	0.6	3.7	13.2	6.8	20.0	. . .	1.5	32.4	36.6	0.89
2086	do	do	do	do	—	6.3	0.5	4.4	13.5	7.7	21.2	. . .	2.0	28.0	39.8	0.70
2087	do	do	do	do		5.5	1.0	1.9	12.6	17.9	30.5	2.1	7.2	26.8	35.0	0.77
2114	do	do	Hard-rolled scoured oak	do	—	8.0	1.9	2.9	15.4	15.0	30.4	6.1	5.5	25.9	32.5	0.80
2115	do	do	do	do	—	8.2	1.4	2.3	14.9	12.9	27.8	4.4	4.4	27.5	33.9	0.81
2116	do	do	Scoured oak	do	+	6.9	1.5	2.5	10.1	12.5	22.6	1.0	6.1	27.7	40.0	0.69
2117	do	do	do	do		7.7	1.5	3.1	9.3	10.7	20.0	0.5	5.1	26.4	42.5	0.62
2118	do	do	do	do		8.9	2.4	1.2	12.5	14.9	27.4	2.8	4.0	30.0	32.2	0.93
2119	do	do	do	do		8.2	1.4	1.5	13.4	11.6	25.0	4.1	2.4	29.5	35.5	0.83
2120	do	do	Texas scoured oak	do	+	8.0	0.5	4.1	15.3	6.5	21.8	0.6	0.6	25.1	40.7	0.62
2121	do	do	do	do		7.7	0.4	3.6	15.3	2.4	17.7	0.4	0.8	29.1	41.6	0.70
2122	do	do	Scoured	do	—	7.6	1.0	4.4	9.4	10.9	20.3	3.2	2.8	26.7	40.7	0.66
2123	do	do	do	do	—	8.9	0.9	3.6	11.6	8.5	20.1	2.3	2.1	23.3	43.8	0.53

2124	. . do	. . do	Scoured oak sole	. do	−	8.1	0.5	1.9	14.7	6.7	21.4	1.0	0.5	30.9	37.4	0.82
2125	. . do	. . do	. . . do	. do	−	7.7	0.4	1.5	10.9	7.6	18.5	1.2	1.2	31.1	40.9	0.76
2126	Baltimore, Md.	. . do	Scoured oak	. do	+	7.2	1.4	1.6	14.8	19.5	34.3	4.9	9.6	23.6	33.0	0.72
2127	. . . do	. . do	. . . do	. do	+	7.4	1.0	4.1	13.1	14.8	27.9	2.1	6.0	25.3	35.0	0.72
2128	. . . do	. . do	Texas scoured oak	. do	+	8.2	0.6	3.4	11.9	7.5	19.4	0.3	1.6	32.3	36.4	0.88
2129	. . . do	. . do	. . . do	. do	+	8.9	0.4	2.0	13.6	5.9	10.5	. . .	1.4	30.0	39.3	0.76
2130	. . . do	. . do	Scoured oak	. do	+	8.8	1.5	1.0	13.6	18.7	32.3	4.5	3.5	25.2	32.4	0.78
2131	. . . do	. . do	Hemlock sole	Hemlock	−	8.3	2.5	1.3	9.3	22.1	31.4	5.7	12.4	25.7	33.0	0.78
2132	. . . do	. . do	. . . do	. do	−	7.6	1.6	1.6	9.7	18.1	27.8	6.4	6.4	24.2	38.5	0.63
2133	. . . do	. . do	Union sole	Union	−	8.7	1.5	2.5	14.6	13.4	28.0	4.1	5.5	27.4	33.1	0.83
2134	. . . do	. . do	. . . do	. do	−	7.4	2.0	3.7	13.5	11.0	24.5	3.8	5.4	28.5	35.6	0.80
2135	. . . do	. . do	Hemlock sole	Hemlock	−	8.4	1.2	1.2	12.0	17.5	29.5	2.8	10.5	28.9	31.7	0.91
2136	. . . do	. . do	. . . do	. do	−	7.7	0.9	1.1	14.1	14.9	29.0	2.0	8.2	27.3	34.6	0.78
2137	. . . do	. . do	Scoured oak	Oak	+	8.2	0.3	1.3	13.7	6.1	19.8	. . .	1.5	33.1	37.3	0.89
2138	. . do	. . do	. . . do	. do	+	8.2	0.4	1.1	14.0	5.9	19.9	. . .	1.2	31 3	39.2	0.80
2139	. . . do	. . do	. . . do	. do	+	12.3	0.5	0.9	10.9	7.1	18.0	. .	1.2	28.9	39 6	0.73
2140	. . . do	. . do	. . . do	. do	+	7.9	0.5	0.7	10.5	7.3	17.8	. . .	1.5	32.4	40.9	0.79
2141	. . . do	. . do	. . . do	. do	+	8.4	1.2	1.1	13.2	14.5	27.7	1.9	5.9	27.0	35.5	0.76
2142	. . . do	. . do	. . . do	. do	−	8.6	0.9	2.3	12.0	12.6	24.6	2.5	5.6	27.0	37.2	0.73
2143	. . . do	. . do	Vat (no extract) scoured oak	. do	−	7.5	0.3	2.9	11.5	6.1	17.6	. .	1.8	29.5	42.2	0.69
2143k	. . . do	. . . . . .	. . . do	. do	−	7.6	0.3	2.6	12.9	4.7	17.6	. . .	0.5	29.0	42.9	0.68
2295	Alexandria, Va.	July	Vat, chestnut oak extract, scoured oak	. do	+	7.9	0.3	1.9	12.6	4.6	17.2	. . .	0.4	34.2	38.5	0.89
2296	. . . do	. . do	Vat, chestnut oak extract, and quebracho	. do	+	7.3	0.4	2.4	14.4	4.7	19.1	0.3	0.5	34.4	36.5	0.94
2296k	. . . do	. . do	. . . do	. do	+	7.9	0.4	3.7	12.4	5.5	17.9	. . .	0.4	33.3	36.9	0.90
2297	. . . do	. . do	. . . do	. do	+	8.2	0.2	1.5	14.4	6.3	20.7	. . .	0.6	34.4	34.9	0.99
2298	. . . do	. . do	. . . do	. do	+	8.4	0.2	1.8	13.8	5.8	19.6	. . .	0.5	34.8	35.1	0.99
		1909														
9695	St. Louis, Mo.	September	No. 1, Texas oak	. do	+	5.8	0.7	3.6	17.3	9.8	27.1	. . .	2.7	25.4	37.8	0.67
9696	. . . do	. . do	No. 2, union	Union	−	5.1	2.4	5.6	14.7	18.9	33.6	7.5	6.5	25.1	30.3	0.83
9697	. . . do	. . do	No. 3, extract tanned, oak	Oak	+	4.1	1.9	5.6	12 9	13.1	26.0	3 5	. . .	27.1	36.9	0.73
9698	. . . do	. . do	No. 4, oak	. do	−	4.1	1.3	4 1	14.5	12.7	27.2	3.1	3.6	26.8	37.5	0.71
9699	. . . do	. . do	No. 5, extract tanned, union	Union	−	4.2	1.6	2.5	16 2	10.2	26 4	3.9	3 4	28.3	38.3	0.74
9700	. . . do	. . do	No. 6, extract tanned	. do	+	3.4	1.0	4.0	14.2	11.4	25.6	2.9	4.3	29.3	37.4	0.78
9701	. . . do	. . do	No. 7, weighted, hemlock	Hemlock	−	3.6	0 9	1.8	11.7	12.9	24.6	2.1	. . .	27.1	42.6	.64
9702	. . . do	. . do	No. 8, hemlock	. do	−	4.7	1.2	1.9	11.6	17.4	28.7	2.1	5.9	29.7	34.7	0.86
9703	. . . do	. . do	No. 9, extract, union	Union	−	4.2	1.1	2.0	14.2	11.3	25.5	2.7	3.7	28 7	39.3	0.73
9704	. . . do	. . do	No. 10, adulterated, South American dry hide	. . . . . .	−	4.7	2.7	2.9	15.5	21.2	36.7	3.8	2.8	25.8	29.6	0.87
9705	. . . do	. . do	No. 11, belly, oak	Oak	+	5.4	0.5	3.8	11.4	13.0	24.4	. . .	3.7	25.7	40.4	0.64
9706	. . . do	. . do	No. 12, extract, hemlock	Hemlock	−	5.6	0.4	1.4	15.8	7.6	23.4	. . .	. . .	26.2	43.1	0.60
9707	. . . do	. . do	No. 13, so-called oak	Oak	+	6.3	1.5	3.5	9 2	12.2	24.4	4.7	3.6	27.3	38.2	0.71
9708	. . . do	. . do	No. 14, oak	. do	−	4.3	0.7	3.4	6.1	10.6	16.7	. . .	5.2	29.1	46.2	0.63
9709	. . . do	. . do	No. 15, oak back	. do	+	4.8	0.8	4.3	13.7	10.3	24.0	. . .	5.6	26.7	39.9	0.67
9710	. . . do	. . do	No. 16, weighted, hemlock	Hemlock	−	5.7	1.9	2.3	14.9	20.2	35.1	3.4	10.7	24 4	32.2	0.76
9711	. . . do	. . do	No. 17, hemlock	. do	−	4.9	0.9	2.2	14.3	8.6	22.9	1.3	3.1	27.6	42.1	0.66
9712	. . . do	. . do	No. 18, South American dry hide, weighted	. do	−	4.3	1.0	2.9	13.7	17.3	31.0	4.3	5.6	30.0	31.5	0.95
[1]9713	. . . do	. . do	No. 19, best	Chrome	−	4.0	6.7	32.1	0.2	2.5	2.7	. . .	1.4	. . .	47.0	. . .

[1] Sample No. 9713: 5.02 per cent. chromium trioxid in original sample.

ANALYSIS OF LEATHER—(*Continued*)

Sample No.	Place sample was obtained	Time sample was obtained	Description of sample	Tannage claimed	Fluorescence	Moisture Per cent.	Ash Per cent.	Petroleum ether extract Per cent.	Water-soluble material: Tannins Per cent.	Water-soluble material: Non-tannins Per cent.	Water-soluble material: Total soluble Per cent.	Epsom salts Per cent.	Glucose Per cent.	Combined tannins Per cent.	Hide substance Per cent.	Ratio of combined tannins to hide substance
		1909														
[1]9714	St. Louis, Mo.	September	No. 20, best	Chrome	—	2.9	6.0	34.6	0.2	2.9	3.1	...	1.4	...	54.9	...
10035	Portsmouth, Ohio	October	No. 1	Union		5.9	1.5	3.1	13.4	14.5	27.9	4.9	5.5	26.4	36.4	0.73
10036	do	do	No. 2, oak	Oak	+	5.7	0.6	2.1	10.4	13.5	23.9	...	8.6	25.6	42.4	0.60
10037	do	do	No. 3	Union		5.9	0.8	2.5	13.5	9.7	23.2	2.6	2.8	30.1	38.0	0.79
10038	do	do	No. 4	Oak		5.2	0.3	3.5	11.7	7.8	19.5	...	1.2	30.7	40.8	0.75
10039	do	do	No. 5	do		5.8	0.3	1.4	12.0	7.6	19.6	...	1.5	31.0	41.9	0.74
10040	do	do	No. 6	do		5.6	0.4	0.9	8.9	19.6	28.5	0.2	8.0	24.6	40.1	0.60
10041	do	do	No. 7	do		6.4	0.3	1.3	12.2	7.0	19.2	...	0.9	29.4	43.4	0.68
10042	do	do	No. 8	Union		4.8	0.9	2.5	12.1	9.8	21.9	0.2	3.8	28.0	42.5	0.66
10105	Unknown	November	Sole, lot No. 110, iron, not treated	do		5.9	0.4	4.7	9.8	3.7	13.5	...	1.0	28.1	47.5	0.59
10106	do	do	Sole, lot No. 210, iron, treated about 6 per cent.	do	+	6.2	2.3	2.0	10.0	13.5	23.5	0.2	9.2	26.7	41.3	0.65
10361	do	December	No. 12	do		5.6	0.8	1.2	12.0	12.1	24.6	...	0.8	27.3	41.0	0.67
10362	do	do	Dark color	do	+	5.3	0.2	4.3	12 2	5.8	18.0	...	1.4	36.4	35.7	1.01
10363	do	do	do	do	+	5.4	0.3	2.9	10.7	5.9	16.6	...	1.0	40.3	34.5	1.16
10364	do	do	Green yellow cast	Oak	—	4.9	0.3	2.5	14.1	4.3	18.4	...	0.8	31.2	42.7	0.73
10365	do	do	Green yellow, redder than above	do		5.6	0.3	1.4	14.5	4.4	18.9	...	0.9	31.8	42.0	0.75
10367	do	do	Hemlock back	Hemlock		5.6	0.8	3.2	14.4	13.9	28.3	...	9.7	32.4	30.2	1.07
		1910														
15058	Washington, D. C.	January	Oak	do	..	9.3	1.2	1.1	17.8	7.7	25.5	1.2	2.5	29.3	34.5	0.85
		1911														
15543	Alexandria, Va.	February	Scoured oak sole	Oak		7.2	0.2	1.9	13.9	5.3	19.2	...	0.7	34.0	37.5	0.90
20635	Washington, D. C.	October	Flexible oak bend	do		8.2	0.4	3.9	11.7	18.5	30.2	..	10.2	23.5	33.9	0.69
20636	do	do	Oak sole	do	..	8.9	0.2	4.0	12.9	5.3	18.2	.	0.7	26.9	41.8	0.64
		1912														
21764	Portsmouth, Ohio	March		Union		6.3	0.7	2.6	13.0	8.5	21.5	1.9	2.3	27.7	41.6	0.66
21765	do	do		do		5.9	1.0	1.1	11.2	10.1	21.3	3.8	4.2	29.2	42.2	0.69
21766	do	do		do	..	6.8	1.5	2.9	12.5	11.8	24.3	4.6	4.6	27.8	37.9	0.73
21767	do	do		Hemlock	—	5.6	1.9	1.6	13.0	14.4	27.4	2.5	6.9	28.4	36.7	0.77
21768	do	do		Oak		5.9	0.7	2.5	14.8	7.7	22.5	1.5	1.7	28.7	40.1	0.71
	Average					6.6	1.1	3.4	12.8	10.5	23.3	2.7	3.8	28.5	38.2	0.75
	Average in weighted samples											3.0	5.5			

[1] Sample No. 9714: 1.32 per cent. chromium trioxid in original sample; 0.30 per cent. chromium trioxid in water soluble.

The leathers here analyzed were secured from various sources; some were sent by tanners, some by shoemakers, some by sole cutters, and others were purchased from dealers. In some cases it was impossible to learn who tanned the leather; in the other cases the name of the tanner was given by the dealer, or his trade-mark or name appeared on the leather. Beyond this nothing is known as to the source of the leathers.

In the third column the approximate date of receipt of the leather is indicated. It will be observed that many of these samples are 5 or 6 years old. Comparison with samples taken more recently does not indicate material change in tannery practice with respect to loading.

Referring to the tables, the "Moisture" consists of the water which the leather exposed to the air naturally contains in addition to all the water of crystallization of any Glauber's salts, or sodium sulphate, and five-sevenths of the water of crystallization of any Epsom salts, or magnesium sulphate, which may be in the leather.

In the column headed "Ash" are given the residues from burning the leather. These residues include the ignited, dehydrated soluble salts which may have been in the leather, such as Epsom and Glauber's salts.

Parker[1] has shown in an extended investigation that the insoluble ash of sole and harness leathers, even though they be heavily weighted with soluble salts, averages less than 0.2 per cent., and very rarely exceeds 0.3 per cent. As none of these leathers was weighted with insoluble minerals, in those cases where the ash exceeds 0.3 per cent. such excess is included as part of the total water-soluble material and so treated in calculating the combined tannin.

The column headed "Petroleum ether extract" shows the percentage of fats and greases which the various leathers contain.

The "Water soluble material" embraces soluble tannins and non-tannins. The latter include glucose, Epsom salts (minus five-sevenths of its water of crystallization, which is included under moisture), and practically all but about 0.3 per cent. of the ash. The sum of the moisture, insoluble ash (assumed here to

[1] *J. Soc. Chem. Ind.*, 1910, **29**: 315.

be 0.3 per cent.), total water soluble, and the hide substance (calculated from the determination of nitrogen) subtracted from 100 approximately equals the combined tannin, which is combined with hide to form leather.

The figures for Epsom salts show the amount of this salt ($MgSO_4+7H_2O$) present in the air-dried leathers. The column headed "Glucose" shows the amounts of water-free glucose and dextrin which the leathers contained, calculated as dextrose. In the last column is given the ratio of combined tannin to hide; that is, the number of parts of tannin combined with 1 part of hide to form leather substance. As will be seen, this quantity does not vary greatly from 0.7 part. In those cases where it is materially greater, it is probable that the leather contained many difficultly soluble reds, or uncombined tannins which were not completely extracted from the leather.

Summary.

A large majority of the samples examined contained an unnecessary quantity of uncombined tanning material. But little less than $1,000,000 worth of tannin is wasted annually in this way.

Sixty-three per cent. of the leathers examined were weighted with glucose, with Epsom salts, or with both. The quantity of loading varied from 1 to 7.3 per cent. of Epsom salts, with an average of 3 per cent. The maximum quantity of glucose in the loaded leathers was 10.4 per cent. and the average 5.5 per cent. The maximum amount of these loading materials found in any leather was 16 per cent. and the average where both were present was 8 per cent. The results obtained indicate that not less than 12,000,000 pounds of glucose and Epsom salts are sold annually in sole leather to the American people.

The materials add absolutely nothing to the wearing value of the leather and where present in large quantity may positively decrease its wear. Shoes made from these leathers are readily penetrated by water. Loading makes leather more costly, consequently an inferior leather costs more than a good leather.

Leather-making raw materials are wastefully consumed, the product may be inferior, the cost increased, and health is endangered by the prevalent practices of weighting and bleaching sole leather.

ON THE QUESTION OF THE ADULTERATION OF SOLE LEATHER.

By W. H. Teas.

The pamphlet recently issued by the Leather & Paper Laboratory giving analyses of numerous samples of American sole leather, accompanied by comments and criticisms, has been widely copied by the daily press, and the lay readers must have the idea that the American sole leather industry is largely an industry of fraud and adulteration. No fair minded sole leather tanner should object to the publication of the results of analyses of American sole leather, but there is ample ground for objection to academic comments, criticisms, and suggested remedies coming from chemists having no experience in the tanning industry—even though they may be what are known as "Government Experts."

Leather prices have not kept pace with hide prices; a few years since, the selling price of a certain class of leather was easily three times the selling price of the green hides from which the leather was made; to-day the same class of leather sells for about 2 1-3 times the cost of the hides. This is a conservative illustration, and others might be noted in which the difference in ratio is even greater. This condition in regard to leather prices is due not only to the stress of ordinary competition, but also to the fact that all producers of sole leather are not on the same footing as regards hides. Some of the producers of the finished leather are also producers of the raw material, and in sharp competition these producers are frequently satisfied to break even in the tanning department, providing the returns are sufficient to give them the full market price for the raw material which they have turned into leather. In the ordinary competition, all sole leather tanners are confronted with the determination of the leather buyers to keep the price of bottom stock as low as possible, so that the cost of the finished shoes may in turn be kept as low as possible.

Under these conditions, the tanner naturally supplies a leather in accordance with the demand; neither the sole-cutter, nor the shoe maker is deceived, each knows what he is getting; and even in the case of the shoe makers who tan sole leather for their own

consumption, it is not likely that they will voluntarily increase the cost of a certain grade of bottom stock beyond the figure at which it can be bought. The fact that the published analyses show adulteration in only about 60 per cent. of the samples examined, is sufficient indication that the buyer gets what he buys and can get unadulterated leather if he is willing to pay for it. The effect of the pure food law has not been to diminish the sale of ketchup containing benzoate of soda, even though it is marked as containing the preservative; there is a demand for the low-priced article, and as long as the demand exists, the supply will be forthcoming.

Adulteration of leather is generally construed as meaning the weighting of the leather with glucose, Epsom salts, glue, barytes etc., but the authors of the Washington pamphlet include the uncombined tannin in the leather as a form of adulteration. This is certainly a most academic view of the matter, and if this view holds, most of the old style all-vat-tanned leather will have to be classed as adulterated leather. Eliminating the different theories of leather formation, and simply as an illustration, let us designate the point in the tanning operation at which the hide and tannin combine to form a product that will not putrefy, as the saturated state. Then, beyond this saturated state, the addition of tanning material is purely mechanical, but the added material serves to fill and hold up the leather structure so that a plump solid leather results. This so-called saturated state in leather might be better described as the point in the tanning process at which the leather is "struck through." Leather in this condition would probably show very little water-soluble matter, and practically no uncombined tannin. This, according to the Washington standard, would be pure leather, and any addition of tannin, or tan-liquor after the leather is "struck through," is to be regarded as adulteration.

This saturated state is presumably reached at the same point now as it was fifty years ago; the vat tanner of those days allowed his leather to stay in the tanning liquors for, say six months; his leather was "struck through" in probably less than half that time, so that the latter part of his tanning process served to fill up the structure of the leather by means of constantly

strengthened tan-liquors; the solidity and weight thus acquired in the latter stages could be washed out of the finely ground leather, and would now be known as water-soluble material and uncombined tannin. The tanner of to-day gets his leather "struck through" at about the same point as his predecessor, and instead of allowing the mechanical tanning to take place in the vats by means of high barkometer liquors, he frequently accomplishes the mechanical tanning much more quickly by means of extract in a revolving wheel.

So that with the same yield of leather from a given amount of hide, there would be as much uncombined tanning material in the leather of fifty years ago as in the leather of to-day. To say that the uncombined tanning material in leather is a waste, and practically a total loss, betokens a lack of knowledge of tanning operations, and of the production of a merchantable, good-wearing leather.

As to bleaching leather, our Washington experts seem to have overlooked the main purpose of bleaching. Before the days of extracts and when all leather was tanned in all-bark liquors, there was a "scrub-house" in every sole-leather tannery. The leather coming out of the strong tan-liquors, and with more or less insoluble sediment on its surface, was thrown into warm water; and after this treatment had soaked out the excess tanning material in the grain, the leather was then scrubbed so that the grain was freed from excess tannin, the color brightened and made uniform, and the finished and dried leather would then have a pliable grain that would not crack open when the leather was bent. Bleaching superseded the old scrub-house methods before the advent of extracts, simply because it was quicker, less laborious, and gave more uniform results. Simple hot water bleaching has been, and is now occasionally used, but it does not give the uniform results of a soda and acid bleach. If sole leather came out of the vats with the finest, lightest color imaginable, it would still require a bleaching, or a similar treatment, to remove excess tannin from the grain, so that a pliable grain would result in the finished leather. When properly carried out, there is little danger of free acid remaining in the leather, and as there is undoubtedly a loss of weight due to bleaching, the

Government experts should not object to thus decreasing the weight of the overloaded leather.

Everyone knows that the supply of our native barks is insufficient to make the oak, hemlock, and union leathers produced in this country, and the retention of these old names can hardly be called a misbranding of leather. Aside from the colors of the old product, the names "oak," "hemlock," and "union," each implied a leather of certain characteristics as to substance, hardness, pliability and finish; and the old names have followed leathers of the particular characteristics as descriptive of the qualities of the leather, rather than of the tanning materials from which they were made. While the tanning materials of a "hemlock" and a "union" leather of to-day might comprise the same list, yet the "hemlock" leather could not be used for all purposes for which the "union" leather is used. This is not intended as a defense of the few tanners that claim an exclusive bark tannage, and who, notwithstanding the claim, use extracts.

Government experts in another department have discovered that a tanning extract can be made from raisin seeds, and it is presumed that the vast amount of leather that will be made from this new tanning agent, will have to be called "Raisin Leather" in order to comply with the ethical standards of the Leather & Paper Laboratory.

The uninformed public has a vague idea that leather of to-day is not of the quality of by-gone years, and that it is tanned with some new tanning material which is vaguely designated as "acid," and which is supposed to do the tanning in a miraculously short time. Dissemination of one-sided literature cannot help the public mind, and is not fair to the tanner. As has been previously pointed out, the tanner does not get the class of raw material originally to be had from range cattle. The original "Texas" steer was a half-wild beast, with a hide provided by nature to protect him from the elements, and most of the hides came from these fully matured animals. With the development of the meat industry, breeds of cattle bred to produce beef were gradually substituted, and the finer textured hides from these younger cattle are now the chief supply of raw material for our tanners. Aside from this difference in the raw material, the leather of

to-day will compare favorably, class with class, with the leather of years ago. Most of the tanning materials used are simply concentrated juices of woods and barks, generally leached just as the bark is leached in the tannery leach house, and in the majority of tanneries the liquors are applied to the hides along the same lines that have been common tannery practice for years. In a recent test of the water resisting qualities of sole leather, it was found that out of 21 tannages tested, it required more than 168 hours for water to penetrate all but two of the leathers tested. This record could hardly be surpassed by all-vat tanned leather of this, or any other time, and could not be made on the average product of today if glucose-weighted leather was as common as some suppose it to be.

The use of glucose, Epsom salts, etc., in sole leather manufacture can only be controlled by a Federal law prohibiting the practice, and tanners would not object to the prohibition, as this would put them all on the same plane. The shoemakers will not take concerted action on this subject, as the first effect of the prohibition will be to increase the price of some grades of sole leather. A law requiring leather containing glucose, Epsom salts, etc., to be so labeled would not diminish the loading to any extent, as there is always more demand for cheap leather than for high priced leather. Bleaching of leather can hardly be controlled by law, as if the shoemaker receives the leather in an unbleached condition, he will have to soak out the grain of the leather before he can use it on the various machines in his factory. The whole proposition of adulterated leather comes back to the world-old axioms, that human nature does not change, and that the buyer generally gets that for which he pays.

PURE LEATHER LAWS.[1]

Pure shoe and leather laws of the Massachusetts Bay Colony were enacted by the General Court in 1642, a period when the Puritans were disposed to regulate everything from the rising up to the going down of the sun, including the activities of the people, domestic, social and industrial.

[1] *Hide and Leather*, May 31, 1913.

"This Court, taking into serious consideration the several deceits and abuses which in other places have been commonly practiced by tanners, curriers and workers of leather, as also the abuse and inconveniences which accrue to the several members of the Commonwealth by leather not sufficiently tanned, which is occasioned by the negligence and unskillfulness of those several tradesmen which before and after it is in the hands of tanners may be much either furthered or impaired, for the prevention whereof it is decreed and ordered as follows,"—so the General Court of 1642 declared, and then it went on to order:

"That no person shall buy, bargain or contract for, or bespeak any hide in the hair, but only such persons as have or do exercise the art of tanning.

"That no person using or occupying the feat or mystery of butcher, currier or shoemaker shall use or exercise the feat or mystery of tanning."

The effect of these two paragraphs, it is plain, was to forbid any persons but tanners to make leather. Any person other than a tanner who tried to make leather was liable to a fine of 6 shillings 8 pence for each hide tanned.

Furthermore, the Court ordered: "That no butcher shall cut or gash any hide whereby its value shall be impaired on pain of a fine of 12 pence for each cut or gash." Tanners would approve of such pure leather legislation to-day. It would secure to them better pelts.

Then, to compel tanners to make good leather, the Court ordered: "That no person using the feat or mystery of tanner shall place the vats in a tan hill, or other places, where the woozes or leather shall take any unkind heat, or shall put leather in to any hot or warm woozes."

Apparently, the purpose of this paragraph was to forbid tanners to force the tanning of leather by heating it. The penalty for violating this paragraph was a fine of 20 pounds.

The Court furthermore ordered: "That no person using the feat or mystery of tanning shall at any time sell or offer for sale any kind of leather which shall be insufficiently tanned, or not thoroughly tanned, or which shall not have been after the tanning well and thoroughly dried." The penalty for the viola-

tion of this paragraph was forfeiture of the leather. Evidently, if tanners of 1642 didn't make good leather the government seized it.

Curriers of leather also were dealt with strictly, and in their case the Court provided: "That a person using or occupying the mystery or faculty of currying any kind of leather shall not curry any hide unless it shall be well and perfectly tanned and thoroughly dried. He shall not use any deceitful or subtle mixture, thing or way to corrupt or hurt the hide; he shall not curry any hide suitable for sole leather with any other than good stuff, nor any less than the leather will receive. He shall not burn or scald any hide in the currying of it, but shall work the same sufficiently in all points and respects." The penalty for the violation of the terms of this paragraph was forfeiture of the leather.

SEARCHERS AND SEALERS.

To make sure that these very strict laws were carried out, the court authorized each town to appoint one or two honest and skillful men as "searchers and sealers of leather." In case these officials seized any leather, the law required that they, within three days after the seizure, call a jury of six men, "honest and skillful in leather," to view the said leather in the presence of the owner, and to pass judgment on the harm done to it by insufficient tanning or currying, or other violation of the law. The finding of the jury would be submitted to the Court, and penalties would be imposed according to law.

If fines were levied, one-third of the amount was paid to the state, one-third to the town in which the offense was committed, and one-third to the "searcher and sealer" who discovered it. Doubtless, prospects of sharing in the fines made "searchers and sealers" zealous in their work of hunting out insufficiently tanned leather. But the same statute also provided that if they erred in seizing insufficiently tanned leather they were liable to a fine of 40 shillings.

These laws of 1642 tied up the leather trade in about the same way that the Connecticut blue laws tied up the Sunday activities of people of the Nutmeg state. After a few attempts to enforce them, they were abandoned.

BOOK REVIEW.

TANNERS' YEAR BOOK, 1913. Honorary Editors. M. C. Lamb and J. Gordon Parker. Published for the United Tanners' Federations by the Technica Publishing Co., 112 Tower Bridge Road, London, S. E. 178 pp. Price, 3 shillings.

The form and style of the Year Book for 1913 are similar in the main to previous issues. Each signed article has a half-tone portrait of the author. The first 37 pages are occupied with lists of officers and members of the Federations represented, with portraits of the former. Eleven pages of reports follow, and then 24 pages of general statistics. The signed articles are as follows:

	PAGES
The Acid Deliming Process, Prof. Proctor	5
Old Leadenhall Market, Illustrated, H. O. Hinton	3
Fellmonger's Problems and Possibilities, A. W. Street	4
The Government Contract for Navy Boots, Henry Miers	2
The Hat-leather Trade, W. Ruttenan	3½
Waste and Want, John T. Day	4
Industrial Strife and Industrial Efficiency, Chas. E. Parker	5
The Graphical Method of Recording Results, Illustrated, J. R. Blockley	9
Sampling of Liquid Tanning Extracts for Analysis, Andrew Turnbull	1
The Mimosa Bark Industry of South Africa, Illustrated, J. Gordon Parker	6
A Plea for the Chemist, S. B. Taylor	2
An Artificial Tannin, E. Stiasny	4
The Progress of Chrome Tanning in England, W. P. Cross	5
The Fellmongers Association, G. W. Russell	1
The Leather Measurement Question, E. C. H. Morris	5
The Leather and Hide Trades' Provident and Benevolent Institution, J. H. Wilks	1
Notes on the Theory of Fatliquoring, J. Bernard Salomon	3
The Soaking of Sheep Skins, J. T. Jackson	6
Hides and Skins, R. Ashton	7
Theory and Practice, T. H. Davies	6
The Analysis of Various Indian Tanned Hides, M. C. Lamb	5
A Resumé of the Principal Publications on the Principles of Leather Manufacture, Stanley Hirst	8

It is rather surprising that the only articles noted at any length in the resumé which closes the book are those by British writers. No leather man disputes the high place held by English leather chemists, but they are not the only ones who have published important papers in the past year.

Several of the signed papers will be reprinted in future issues of the JOURNAL, with abstracts of a number of others.

PROCTER RESEARCH LABORATORY.

Mr. H. C. Reed, Chairman of the Committee of the Association to solicit funds in aid of the Procter Research Laboratory project, has received and forwarded to the JOURNAL the following paper, which is self-explanatory.

SCHEME FOR THE CONTROL AND MANAGEMENT OF THE PROCTER INTERNATIONAL RESEARCH LABORATORY.

As approved by the Council of Leeds University.

1. *Object.* The object of the Institution is to provide international facilities for research on the scientific principles on which leather manufacture depends, and not for the practical development of special manufacturing methods, or for commercial investigations, which are the proper subjects of private laboratories or of the Tanning Schools. Since, however, cases may arise involving both scientific and commercial considerations, the Governing Body shall have power to permit (but not to prescribe) researches of immediate technical importance. The results of all researches shall be published in such a form that they are accessible to the public, and may be reprinted without copyright by technical journals throughout the world with acknowledgment of their source.

2. *Honorary Director and Assistant.* To facilitate the carrying out of these objects, an Honorary Director shall be appointed, who shall receive no salary, but shall be entitled to the repayment of necessary personal and other expenses, including traveling expenses incurred in the carrying out of his researches and duties as Director, to a sum not exceeding fifty pounds per annum.

A qualified assistant shall be appointed capable of carrying out experimental work under the Director, and of taking charge of the laboratory, and of supervising the Research Fellows during the absence of the Director, at a salary to be subsequently determined by the Governing Authority.

The first Honorary Director shall be Prof. H. R. Procter, who shall continue to hold office so long as he is able and willing to continue his scientific work. Subsequent appointments to these posts shall be made as determined by the Governing Authority.

3. *The Governing Authority* shall be the Council of the Uni-

versity of Leeds as Trustees in whom the building and all funds shall be vested, assisted by and in conjunction with an Advisory Committee, which shall appoint from time to time from its number or by co-optation an Executive Committee of men of scientific attainment, including, *ex-officio,* the Pro-Chancellor and Vice-Chancellor of Leeds University and the Honorary Director, and not exceeding seven in number, which shall have power to report direct to the Council on all matters affecting the management of the Laboratory, the election of Research Fellows, and the suitability of proposed researches, subject to the rules from time to time laid down by the Advisory Committee and the Council.

4. *The Advisory Committee* shall include *ex-officio* the Pro-Chancellor and Vice-Chancellor of the University of Leeds, and the Honorary Director and representatives of the following bodies, viz.:

Two representatives from the Senate of the University, of whom one shall be the Professor of the Chemistry of Leather Manufacture.

One representative from each Section of the International Association of Leather Trades Chemists which includes 50 or more members.

One representative of the American Association of Leather Chemists.

And representatives of such Guilds, Federations or other bodies who have made such contributions to the Laboratory fund, either in capital sums or annual subscriptions, as may entitle them in the opinion of the existing Executive Committee of the Building Fund, or subsequently of the Advisory Committee, to representation.

5. The fund raised shall be applied first to the erection and equipment of a suitable laboratory on plans approved and agreed mutually by the Council of Leeds University and the Committee of the fund, and on a site provided by the Council of Leeds University; and the balance of the fund after the building and equipment of the laboratory shall be handed over to the Council of the University by the Committee of the Fund, and thenceforth be vested in them as trustees, and the income arising from it, together with any received as annual subscriptions or grants to the

Research Laboratory shall be devoted in the first instance to the maintenance of the Laboratory, the supply of necessary chemicals and apparatus, and the payment of the salary of the Assistant, and of the Director's expenses as stated in Par. 2, and the balance, together with any grants, subscriptions or endowments given specially for the purpose, shall be devoted to the creation of Research Fellowships, tenable by qualified chemists of all nationalities, without distinction or preference as may from time to time be decided by the Council in conjunction with the Advisory Committee.

ABSTRACTS.

Hides and Skins in South China. CONSUL G. E. ANDERSON, Hongkong, in *Consular Reports*. Goat, cow and buffalo skins have been shipped to U. S. in considerable quantities since 1908. Formerly these came chiefly from northern ports, but the shipments from the south are increasing. Many hides go to Singapore and are re-imported as leather. Some tanning is done locally. Hides for export are usually imported by a single firm in Hongkong which represents a family in the business for five generations and which practically has a monopoly of the business. They come in the raw state and are sold to local dealers who cure them for export. About 3,800 pieces (1,000 piculs or 133,333 pounds of salted cowhides per month are marketed in Hongkong, about 800 of which are from local slaugthering. Prices at present (March 22) are unusually high, the price for Hongkong hides being $37 local currency or $17 gold per picul of 133⅓ pounds, which includes 3½ to 4 pieces, and the price for hides from other points being $32 local currency, or $14.70 gold per picul, which includes 4 to 4½ pieces. Buffalo hides from the interior are to be had in comparatively small quantities and at present sell at fully 20 per cent. under prices for cowhides. The supply of dry hides is comparatively limited, lots of 1,000 to 1,200 coming on the market from time to time at from $65 to $70 local currency or $29.90 to $32.20 gold per picul, which includes 7 pieces. Dried hides from other points at present bring from $55 to $60 local currency, or from $25.30 to $27.60 gold per picul, a picul including about 7 pieces. Dried buffalo hides are to be had, but they are generally considered of inferior quality and are not exported at present.

Sulphite-Cellulose Extracts. SIG. SAXE. *Hide and Leather*, June 7, 1913. In spite of the small quantities of true tannin present in sulphite-cellulose liquors, they combine with hide to form leather. The real character of their action is not yet understood. Not only may these extracts be used in blends for tannage, but also to very good advantage

in "extracting" heavy leather. Mr. Saxe takes exception to the statement of Messrs. Veitch & Rogers (see their paper in this number) that the use of these extracts has been crowned at most with indifferent success. Many tanners who began the use of the new extract several years ago continue to use them, and are making good leather. Sulphite-cellulose extract may properly replace both glucose and Epsom salts as a filler. Some leathers are improved in color by this material. Steady increase in the sales shows that the extract has merit.

Spanish Leather Trade Congress. *L. T. Rev.*, May 21, 1913. The second Congress assembled at Saragossa, April 23, 1913, continuing 5 days. Twenty-two topics were discussed. Many of these relate to prices, taxes and allied subjects. In considering steps that should be taken to improve the condition of hides from the provinces, it was recommended that the use of the hammer for flaying be made compulsory; that the killing of pregnant animals be prohibited; that stringent measures be adopted to eradicate tick and other like sources of injury, and that branding be discouraged in all possible ways.

The Tannery School soon to be opened in Barcelona will be under the care of an association of leather manufacturers. Certificates of analysis issued by this school will be considered official. Firms selling extracts will be required to furnish certified analysis of their products. It was resolved that analyses should also be given with oils, dyes and other materials. The right of the user of leather to demand from the tanner a statement of the purity of leather, or of the amount of adulterants contained, was asserted by the Congress, and in cases of dispute the Barcelona School is to furnish a certified analysis which shall be accepted as final evidence. The advantages of chrome tannage were recognized, and tanners were advised to make a special study of chrome processes. A prize of 1,000 pesetas (about $200) was offered for the best treatise on tanning written in Spanish in the course of the year.

Employment of Emulsifying Oils and Emulsions in the Tannery. U. J. THUAU, Le Cuir, vi, 290-3. These oils are used in the stuffing of chrome goat and box-calf, combination tannages like dongola. or vegetable leathers; also to facilitate vegetable tannage in the drum and to aid in the drying of finished leathers. Several theories of the nature of emulsions are briefly stated. Four classes of emulsions are used in the tannery: 1, those having for a base sulpho-ricinate of soda (Turkey red oil) or other sulphonated fatty acids; 2, those having soap only as a base; 3, those made with solvents of oils and fatty acids, and 4, those in which both Turkey red oil and solvents are used, sometimes also including fatty acids and soaps. To class 1 belongs sulphonated neats-foot oil. It is often solid, and does not keep long without change. It does not form very stable emulsions. Emulsions made with Turkey red oil and an animal or vegetable oil are never stable, in spite of careful preparation they always separate in a few weeks; by the addition of a proper amount

of mineral oil, it is possible to secure stability. A very good emulsifying oil for the stuffing of chrome leather, giving a very stable emulsion with water showed the following percentages on analysis: water, 28; sulphonated fatty acids, 3.9; ash, 3.1; neutral saponifiable oil, 42.2; mineral oil, 22.8. This oil was made with 40 parts Turkey red oil, (50% water), 37 parts neats-foot oil and 23 parts mineral oil. The Turkey red and mineral oils are intimately mixed in a shaker. The neats-foot is then added slowly with continued agitation.

In the last stage of making Turkey red oil, the addition of strong alkali gives the oil a gelatinous consistency. It is best to add the soda in small portions. Each addition makes the mass milky, and it must be shaken until it clears. There are many formulas for emulsions of this class, suitable for dongola and certain chrome leathers. Three are given, made in the same manner as that already described.

	I	II	III
Turkey red oil (50%)	15	15	15
mineral oil	30	25	20
castor oil	15		
cod oil		20	
neats-foot oil			15
fish oil			10

Class 2, soap emulsions are less stable than Class 1, whether they are made with a soap and an animal or vegetable oil, or whether a mineral oil be added. Fat-liquors for chrome made in this way give doubtful results, although it has long been the practice to add egg-yolk, which much facilitates the emulsion. Some products in the market falsely called soluble oils are made with soap, and are incapable of yielding stable emulsions. There is a kind of emulsion which gives good results that may be placed in this group. The active body in this case is the amide of stearic acid, which has been made into a paste with water. Any oil except olein mixed with this aqueous paste will make a very fine and stable emulsion.

A type of Class 3 is the mixture of oleic acid, ammonia and alcohol. The acid is dissolved in either grain or wood alcohol, and a little ammonia added with shaking. Water is then added with stirring until a thick mass is formed. A fat-liquor for box-calf gave the following percentages on analysis: water, 48.4; alcohol, 10; ammonia, 5.2; saponifiable oil (neats-foot), 9.8; oleic acid, 26.6. Similar emulsions may be made with other fatty acids, or other solvents may be used, as carbon disulphide, carbon tetrachloride, benzine, etc. With these emulsions, insoluble mineral matter may be held in suspension. To an emulsion such as that described, finely ground silicates mixed with benzine may be added, up to 30% of silicates. Another emulsion of this class: olein 90 parts, ammonia (22°) 27, alcohol (95°) 15, oleic acid 5, peanut oil 9, potash 0.8, solution of caustic soda of 36°, 0.4. The materials are boiled for an hour with a minimum of water. Another mixture (soluble) has alcohol 10, water 80, oleic acid 30.

alcoholic solution of ammonia (10% ammonia) 15, vaseline oil (sp. gr. 0.885), 60.

Emulsions of Class 4 are the best and most stable. An intimate mixture of Turkey red oil and carbon tetrachloride is soluble in water. This mixture in solution in water may be used to degrease hides and leather. Mixtures of Turkey red oil with benzine, carbon disulphide, etc. are also soluble in water. In general, other oils dissolved in a solvent and mixed with Turkey red oil make good emulsions. If it is necessary to make an emulsion with much water it may be worth while to add a gum, glucose or beaten white of egg. L. B.

Practical Method of Emulsifying Fish Oils. U. J. THUAU, *Le Cuir* VI 367. To emulsify cod oil, boil 6 parts of Irish moss 20 minutes with water enough to make 440 parts of decoction; strain and boil with 250 parts oil. Agitate during cooling. This emulsion is fairly stable, but ferments easily. To prevent fermentation, salicylic acid, etc., may be used. Agar-agar may be substituted for Irish moss. L. B.

Oils, Fats and Solvents in the Manufacture of Leather. S. M. *Les Matieres Grasses*, Vol. 5, pp. 2,939 and 2,982. The use of fish oil, sulphonated oils, mineral oils and wool oil is noted. The injurious action of certain solvents employed in making blackings, dressings, etc., is well known. Turpentine is often so used. It injures the fiber of the leather. Some makers guarantee their products free from turpentine and other harmful ingredients. A French chemist subjected samples of leather to the action of various solvents in sealed vessels for one month, with results as follows: turpentine, hard, with increase of weight; water, supple, slight loss of weight; carbon tetrachloride and naphtha, a little hard, due to loss of fat; amyl acetate, quite soft and flexible. The use of sulphate of lead as a whitener is deprecated because of its poisonous character. L. B.

The Determination of Free Sulphuric Acid in Leather. *Le Cuir*, VI 379-81. Three principal methods have been proposed, that of Balland and Maljean, that of Jean and that of Procter and Searle. Messrs. Paessler and Sluyter have described a modification of the first-mentioned. Before dissolving the ash in nitric acid they add bromine water to reoxidize the products of reduction. (One would think nitric acid would suffice. tr.) Mr. G. Rehbein burns the leather in a current of oxygen in a combustion tube. Two or three grams of finely divided leather are placed in a platinum or porcelain boat in a combustion tube 2 ft. long and ¾ in. in diameter.

Dried and filtered oxygen is led into the tube. A platinum spiral surrounding a mass of quartz and platinized quartz is placed near the other end. The gas after passing through the tube is led into a flask containing water and 1 gram of sodium peroxide free from SO_3. A slow current of O is sent through and the platinum spiral heated to bright red-

ness. As soon as the leather begins to burn a strong current of O is turned on. When the combustion is nearly finished the boat is heated strongly to decompose any sulphates which are only decomposable at a white heat. When the combustion is finished and all the gaseous products have been driven into the alkaline liquid, the liquid is acidified with hydrochloric acid and the SO_3 precipitated with $BaCl_2$. The author says that free SO_3 in extracts may be determined by this method, allowance being made for the SO_2 of bisulphites and the SO_3 of bisulphates. In order to allow for the SO_3 due to the sulphur contained in untanned hide, he made a number of determinations on leather known to have no added SO_3 or sulphates. An average result is 0.18% SO_3. The author describes check determinations on samples having known added quantities of SO_3, the results indicating that the method is a good one. Experiments with sulphates of iron, aluminum, chromium and lead show that the SO_3 from these is completely driven out by the method (and would, therefore, seem to appear as free SO_3. tr.) The SO_3 of magnesium sulphate is driven out to the extent of 64%, while that of calcium sulphate and the sulphates of sodium and potassium are not expelled to any appreciable extent. L. B.

Sulphuric Acid in Leathers. F. QUANNONE. *Bourse aux Cuirs de Liége*, May 18 and 25, 1913. The author points out the lack of concordance in results in the determination of free SO_3 in leather. He gives the figures of the international commission, varying from 0.05 to 0.38%. He quotes Sody and Eitner in support of the opinion that percentages of free SO_3 up to 1% in heavy leather do not injure it, and protests against objection being made to the presence of combined SO_3. L. B.

PATENTS.

Ovens for Treating Leather. British Patent, No. 1,464. W. R. SMITH, Buffalo, N. Y. Invention for baking enamel on patent leather.

Leather Evening and Grading Machine. U. S. Patent, No. 1,058,623. ELMER P. NICHOLS, Manchester, N. H.

Glazing and Rolling Machine. British Patent, No. 29,055. J. N. DEAN, Stockport, Lancashire.

Evaporating Apparatus. U. S. Patent, No. 1,060,607. PAUL KESTNER, Lille, France.

Process for Treating Iron Tanned Leather. U. S. Patent, No. 1,061,597. JOSEPH BYSTRON, Teschen, Austria-Hungary.

Hide-Splitting Machine. U. S. Patents, Nos. 1,058,962 and 1,061,604. JOSEPH H. GAY, Newark, N. J.

Treating Waste Liquors from Tanneries. British Patent, No. 2,190. J. FORSTER, Warrington, England. The process consists essentially in mixing the liquors after filtration and then evaporating them to dryness.

This is the same gentleman who patented a process of tannage in which the hides are moved instead of the liquors (*Journal*, 1912, p. 394), and a process of leaching in which the flow circuit is fixed and the material is transferred from one leach to the next (*Journal*, 1912, p. 504).

Machine for Treating Hides, Skins and Leather. U. S. Patent, No. 1,062,-026. DANIEL P. O'BRIEN, Woburn, Mass.

Hollow Work-support for Leather-working Machines. U. S. Patent, No. 1,058, 749. HENRY A. HOLDER, Lynn, Mass.

Knife-cylinder for Hide-working Machine. U S. Patent, No. 1,062,617. JACOB STRYKER, Somerville, Mass.

Leather Product and Process of Manufacturing the Same. U. S. Patent, 1,064,048. CARL BRANDT, Norwood, Mass. A process of making variegated fancy leathers.

Process for the Production of Leather-board Stock. U. S. Patent, No. 1,063,958. ALBERT L. CLAPP, Braintree, Mass. The materials used are wood-flour, oil and shredded leather.

Process of Producing Tanning Extracts. U. S. Patent, 1,063,428. GIUSEPPE GIANOLI, Milan, Italy, assignor to Lepitit, Dollfus and Gansser. Waste sulphite-cellulose liquor is freed from sulphurous acid and lime compounds and added to crude quebracho extract, the combination being then heated to from 95° to 115° C.

Process of Making Leather Flexible. U. S. Patent, No. 1,062,947. GEORGE BASLER, Lynn, Mass. The grain side is treated with a solvent and the leather is then mechanically worked.

Process of Preparing a Tanning Extract. French Patent, No. 448,064. W H. PHILIPPI. The process combines sulphite-cellulose liquor, freed from lime by the use of soda, with chrome alum and chromium hydroxide. The spent liquors are strengthened by the addition of strong liquor, and the tendency of acid to accumulate in the bath is met by additional chromium hydroxide. The method is described in *Le Cuir*, March 15, 1913. No means of getting rid of the alkaline salts which accumulate in the liquors is mentioned.

Imitation Leather, French Patent, No. 449,213. The patentee is a German association. The process is described in *Le Cuir* for May 15, 1913. It consists in growing certain micro-organisms on appropriate media in thick membranes so formed. The organisms may grow to a thickness of a foot, from which tanned "leather" nearly 1 cm. thick may be made. (Such growths as often occur in tan vats may become so heavy as to resemble leather very closely in appearance, the surface looking very much like the grain side of cowhide. Tr.).

Method of Tanning the Skins of Sharks, etc. British Patent, No. 3,481. K. BENDIXEN and others, Copenhagen. Process described in much detail and with many alternatives.

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LLOYD BALDERSTON . . . . Associate Editor

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ADOPTION OF CHANGES IN METHOD OF TANNIN ANALYSIS.

NEW YORK, July 1, 1913.

MR. W. K. ALSOP, Editor,
Ridgway, Penna.

DEAR SIR:

Following is the vote on the proposed changes in the Official Method of the A. L. C. A.:

Total votes cast	36
Necessary to adopt	24
Affirmative votes	29
Negative votes	7

I therefore declare the proposed changes adopted and that they will be effective on publication of this notice (August 1, 1913).

Yours truly, H. C. REED, *Secretary*.

ELECTIONS.

ACTIVE

Frederic W. Ames, c/o Graton & Knight Mfg. Co., Worcester, Mass.

Alexander N. Dubois, 308 North Ninth Street, Wilmington, North Carolina.

Frederic L. Hilbert, c/o Green & Hickey Leather Co., Winchendon, Mass.

ASSOCIATE.

Josiah M. Fiske, 41 Park Row, New York City, N. Y.

NOTE ON THE ANALYSIS OF TANNINS, IV.

By L. E. Levi and Aug. C. Orthmann.

Making Reagent No. 33.

To make the reagent great care must be taken and only chemicals of known purity and strength should be used. The authors analyzed all chemicals used and in some cases several recrystallizations of the chemicals were necessary.

In making reagent No. 33 we tried to get it free from sodium and potassium salts (sulphates and chlorides) in order to get as nearly as possible a pure solution of the supposed compound.

$$Cr_2SO_4(C_2H_3O_2)_2CrO_4.$$

Such a quantity as should be diluted to about 2,000 cc. and of proper strength is made as follows:

In a 1,000 cc. porcelain casserole place 29.45 grams potassium bichromate, which is dissolved in a very small quantity of pure distilled water, to this is added very slowly 39.2 grams sulphuric acid, 100 per cent., or its equivalent, the resulting solution is cooled to about 15° C. and ethyl alcohol is added very slowly with continuous stirring. Enough ethyl alcohol is added to reduce all the potassium bichromate present to chromium sulphate according to the following equation:

$$K_2Cr_2O_7 + 4H_2SO_4 + 3C_2H_5OH = Cr_2(SO_4)_3 + K_2SO_4 + 3CH_3CHO + 7H_2O.$$

The solution is then boiled to drive off all traces of the ethyl

aldehyde formed, after which it is cooled and diluted to 1,000 cc. with distilled water. A stock solution of this can be made for future use, say 2 or 3 times the amount given, and placed in a well-stoppered bottle.

Take 100 cc. of the above solution, place into a 1,000 cc. beaker and add about 700 cc. distilled water, bring to a boil, add ammonium hydroxide to a very slight excess and boil for one-half hour or until all excess of ammonium hydroxide is driven off. Remove from flame and allow precipitate to settle. In the meantime prepare a 5-inch funnel with a filter paper large enough to hold all the precipitate, decant the clear liquor into the filter and when all supernatant water is decanted throw all the precipitate onto the filter and immediately after the precipitate has drained wash with boiling hot distilled water free from carbon dioxide.

To get distilled water free from carbon dioxide the authors redistilled all water over barium hydroxide.

Wash the precipitate of chromium hydroxide until free from sulphates and chlorides. Then remove most of the precipitate to a 1,000 cc. casserole with a platinum or porcelain spatula and wash the last traces of the precipitate remaining on the filter into the casserole with a few cc. of hot water.

As the above 100 cc. of chromium sulphate solution is calculated to give 2.06 grams chromium hydroxide this is repeated until 20.6 grams of chromium hydroxide, the calculated amount, has been obtained or until 1,000 cc. of the above stock solution of chromium sulphate have been used up, which is equal to 20.6 grams of chromium hydroxide.

The authors preferred to use but 100 cc. of the chromium sulphate solution at one time, on account of the bulkiness of the precipitate of $Cr_2(OH)_6$ which if taken in larger quantities makes it more difficult to wash and consumes too much time.

To 20.6 grams of chromium hydroxide add 19.6 grams of sulphuric acid 100 per cent. or its equivalent quantity of lower per cent. After adding the sulphuric acid place the casserole over a burner and boil the mixture until all is dissolved. This operation requires some time. The mixture must be boiled down to about 35 to 50 cc. Care must be taken or a loss will occur due to sputtering.

When all chromium hydroxide is in solution add about 700-800 cc. of distilled water and bring to a boil, then add 25.5 grams of barium acetate, $Ba(C_2H_3O_2)_2$, in solution (dissolve in about 200 cc. water and add slowly). After all is added boil the solution for about 15 minutes longer then add 10 grams CrO_3 highest purity and boil for five minutes and dilute to 2,000 cc.; then allow to cool over night. Next morning filter off the clear solution but do not wash the precipitate, discard same and place filtrate in a well-stoppered bottle. Reagent is now ready for use.

The reactions taking place are as follows:

$$Cr_2(SO_4)_3 + 6NH_4OH = Cr_2(OH)_6 + 3(NH_4)_2SO_4,$$
$$Cr_2(OH)_6 + 2H_2SO_4 = Cr_2(SO_4)_2(OH)_2 + 4H_2O,$$
$$Cr_2(SO_4)_2(OH)_2 + Ba(C_2H_3O_2)_2 = Cr_2SO_4(C_2H_3O_2)_2(OH)_2 + BaSO_4,$$
$$Cr_2SO_4(C_2H_3O_2)_2(OH)_2 + CrO_3 = Cr_2SO_4(C_2H_3O_2)_2CrO_4 + H_2O.$$

Analysis of Tanning Materials.

Such quantity should be taken as will give from 0.35 to 0.45 gram tannin per 100 cc. of solution.

The materials should be sampled, weighed and diluted in exactly the same manner as in the Official Method of the American Leather Chemists Association for Tannin Analysis.

Then from the soluble solids 10 cc. is taken and placed into a 50 cc. beaker and five cc. of Reagent No. 33 is added and thoroughly mixed, the beaker being covered with a watch glass and let stand over night (at least 12 hours) then filter through a 11 cm. folded filter into a 300 cc. Florence flask, wash with distilled water at room temperature until all the precipitate is washed free from reagent, which requires about 100 cc. water. Discard the precipitate as only the filtrate is used in our method.

* The objection to the direct method, *i. e.*, determination of Cr_2O_3 in the precipitate, is the burning of the filter containing the precipitate and fusing with a suitable flux which requires more time and a greater chance of error is involved. The method of oxidizing filter and precipitate in one operation by placing both together in a flask, adding water and oxidizing with sodium peroxide was tried. This gave low results, probably due to a large amount of filter paper present, forming organic products which have an influence upon the titration with sodium thiosulphate.

Determine Cr_2O_3 in filtrate in the following manner:

To the contents of the flask add about 5 grams of sodium peroxide shaking the flask well, then boil until all free oxygen has been driven off which requires about one-half to one hour. Then dilute to about 150 cc. and cool to about 15° C. When cool, slowly add an excess of cold dilute sulphuric acid to convert the chromate to chromic acid, then cool again to 15° C. and add one gram of potassium iodide in solution and immediately titrate with N/10 sodium thiosulphate solution using starch as indicator, which is the usual iodometric method for the determination of chromates. At the same time oxidize 5 cc. of the reagent and carry through in the same manner.

The difference between the two titrations is multiplied by 0.005743317x100 and divided by the amount of material taken to get the per cent.

Example:

Ten grams tanning material was diluted to 1,000 cc. to ten cc. of this filtered solution was added five cc. reagent No. 33. Ten cc. solution contains one gram material

5 cc. reagent No. 33 required.............	25.4 cc. N/10 hypo
Filtrate from mixture required	19.0 cc. N/10 hypo
	6.4 cc. N/10 hypo

used up in reaction.

Then $0.005743 \times 6.4 = 0.036756$ gram tannin

$$\frac{0.036756 \times 100}{0.1} = 36.756 \text{ per cent. tannin.}$$

To obtain the tannin factor for 1 cc. N/10 thiosulphate.

The precipitate obtained with the reagent No. 33 and pure tannic acid contained 66.3729 per cent. Cr_2O_3. (See *J. A. L. C. A.*, Oct., 1911, pages 475, 476.) This was calculated from tannic acid $C_{14}H_{10}O_9$ to the hypothetical monoglucoside $C_{20}H_{20}O_{14}$ giving 44.1571 per cent. Cr_2O_3 since 1 cc. N/10 hypo is equal to 0.002536 gram Cr_2O_3, 1 cc. N/10 hypo would be equal to 0.00574317 gram $C_{20}H_{20}O_{14}$ (tannin); the factor used throughout this work.

In our last paper (*J. A. L. C. A.*, Apr., 1913, pages 162-3)

it will be noticed that the insolubles formed by sulfite cellulose ext. "B" are higher than those (where formed) formed by S. C. Ext. "A." This is probably due to the large amount of aluminum compound present in S. C. Ext. "B," the analysis of which is as follows:

S. C. Ext. "A"	S. C. Ext. "B"
Al_2O_3 = 0.67 per cent.	Al_2O_3 = 1.90 per cent.

In this, our fourth article (Note on the Analysis of Tannins, I, II and III, *J. A. L. C. A.*, Oct., 1911; Jan., 1913; April, 1913), we lay before the chemists a new method for the analysis of tannins and at the same time a method for the determination of sulphite cellulose extracts by difference. The reagent No. 33 does not precipitate the sulphite cellulose extracts while the actual tannins are precipitated.

The difference between the hide powder method and the reagent No. 33 method gives the amount of sulphite cellulose extract present. The last and concluding article with reagent No. 33 will be published shortly and will treat of the application of reagent No. 33 in the analysis of used tanning liquors containing more acid and less tannins than the extracts as placed upon the market.

ANALYSES OF SOME SAMPLES OF WOOL GREASE.

By Charles Eachus.

Wool grease is handled extensively in the leather industry and many other large industries of this country. It comes from many different sources here and in Europe, and an analysis is seldom asked for. Some tanners and textile men think that they can use only a certain brand, and any other will ruin their goods. This may be true to some extent, and it is a fact that wool grease sometimes causes trouble, but it is chiefly due to the way it is used. For several years, many of the troubles of the currying department in tanneries, have been attributed to wool grease, when as a rule something else was responsible. Chemical analyses show little about the qualities of wool grease, except the percentages of water, dirt, and unsaponifiable. The writer has had occasion to make comparative analyses of different

samples and gives below some of the more commonplace determinations. The principal value of these lies in the fact that the samples were genuine, and the determinations were carefully made by the same methods, and at the same time.

Sample	Color	Water	Melting-point ° F.	Unsaponifiable petroleum ether	Unsaponifiable sulphuric ether	Iodine value	Free fatty acids as oleic
1	Dark brown	0.37	107	25.03	37.45	28.02	25.75
2	Light brown	0.97	101	25.84	37.66	24.96	20.96
3	Light yellowish brown	4.10	104	30.17	43.14	20.53	7.17
4	Reddish brown	0.56	108	28.89	39.14	22.96	20.57
5	Dark brown	0.94	102	33.52	44.63	27.04	18.45
6	Brown	0.60	114	28.06	41.74	24.63	16.16
7	Brown	0.59	105	27.60	43.68	21.48	9.39

The sources of the samples are as follows:

1. Dark English, made by scouring the wool with soap and cutting the suds.
2. Light English, made by scouring and cutting suds.
3. Belgian, made by extracting the wool with naphtha.
4. American, made by scouring and cutting suds.
5. French, made by scouring and cutting suds
6. German, made by scouring and cutting suds.
7. American, made by extracting the wool with naphtha.

The analyses are calculated on water free basis, and the water in the Belgian sample was unusually high, probably accounting for its light color. The naphtha extracted samples are the purest wool grease uncontaminated by the fatty acids from the soaps used in scouring, and consequently the free fatty acids and iodine values are lowest in these samples. There is a wide variation in melting points, that is hard to account for, but the melting point of each sample agrees very well with the consistency of the sample.

The unsaponifiable determinations were made by boiling two hours in a flask with alcoholic caustic potash, and shaking out with ether in a separatory funnel. In other words, the same method was used for these samples that would be used in case of a fat that might contain wool grease. It is the writer's experience that the addition of wool grease to another fat increases

the unsaponifiable in direct proportion to the amount of unsaponifiable in the wool grease added.

Petroleum ether apparently dissolves less than 70 per cent. of the alcohols in the unsaponifiable of wool grease, and it would seem that sulphuric ether should be used wherever wool grease is present. The unsaponifiables of these samples were tested for mineral oil and none was found present.

OFFICIAL METHODS OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION.

ANALYSIS OF VEGETABLE MATERIALS CONTAINING TANNIN.

I. RAW AND SPENT MATERIALS.

(1) *Caution:*

Proper care must be taken to prevent any change in the water content of raw materials during the sampling and preliminary operations. (See "General" under Sampling.)

(2) *Preparation of Sample:*

The sample must be ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

(a) The temperature used for drying samples of spent material for grinding must not exceed 60° C.

(b) Samples of raw material too wet to be ground may be dried before grinding as in (a). In this case a preliminary water determination must be made according to (IV) on the sample as received. If the portion of the sample taken for the water determination is in pieces too large to dry properly, it is permissible to reduce these to smaller size as rapidly and with as little loss of water as possible.

(3) *Water Determination:*

Ten grams of the ground material shall be dried in the manner and for the period specified for evaporation and drying in extract analysis (see IV).

(4) *Amount of Sample to be Extracted:*

Such an amount of raw material shall be extracted as will give a solution containing as nearly as practicable 0.4 gram tannin to 100 cc. (not less than 0.375 or more than 0.425). Of spent materials such an amount shall be taken as will give a solution of as nearly as practicable the above concentration.

(5) *Extraction:*

Extraction shall be conducted in an apparatus consisting of a vessel in which water may be boiled and a container for the material to be extracted. This container shall be provided above with a condensation chamber so arranged that the water formed from the condensed steam will drip on the material to be extracted, and provided below with an arrangement of outlets such that the percolate may either be removed from the apparatus or be delivered to the boiling vessel. The boiling vessel must be so connected that it will deliver steam to the condensation chamber and that it may receive the percolate from the container. The condensation water from the condenser must be at approximately the boiling temperature when it comes in contact with the material to be extracted.

The material of which the boiling flask is composed must be inert to the extractive solution. Suitable provision must be made for preventing any of the solid particles of the material from passing into the percolate.

(A) *Woods, Barks and Spent Materials:*

Five hundred cc. of the percolate shall be collected outside in approximately two hours and the extraction continued with 500 cc. for 14 hours longer by the process of continuous extraction with reflux condenser. The applied heat shall be such as to give by condensation approximately 500 cc. in 1½ hours.

(B) *Materials Other than Woods, Barks and Spent:*

Digest the material in the extractor for one hour with water at room temperature and then extract by collecting two liters of percolate outside in approximately 7 hours.

(6) *Analysis:*

The percolate shall be heated to 80° C., be cooled, made to the mark and analyzed according to the official method for extracts.

II. ANALYSIS OF EXTRACTS.

(7) *Amount and Dilution for Analysis:*

(A) *Fluid Extracts:*

Fluid extracts shall be allowed to come to room temperature, be thoroughly mixed, and such quantity weighed for analysis as will give a solution containing as nearly as possible 0.4 gram tannin to 100 cc. (not less than 0.375 nor more than 0.425). Precautions must be taken to prevent loss of moisture during weighing. Dissolve the extract by washing it into a liter flask with 900 cc. of distilled water at 85° C.

Cooling:

(a) The solutions prepared as above shall be cooled rapidly to 20° C. with water at a temperature of not less than 19° C., be made to the mark with water at 20° C. and the analysis proceeded with at once, or

(b) The solution shall be allowed to stand over night, the temperature of the solution not being permitted to go below 20° C., be brought to 20° C. with water at not less than 19° C., be made to the mark with water at 20° C. and the analysis proceeded with.

(B) *Solid and Powdered Extracts:*

Such an amount of solid or powdered extract as will give a solution of the strength called for under liquid extracts shall be weighed in a beaker with proper precautions to prevent change of moisture. One hundred cc. of distilled water at 85° C. shall be added to the extract and the mixture placed on the water-bath, heated and stirred until a homogeneous solution is obtained. When dissolved, the solution shall immediately be washed into a liter flask with 800 cc. of distilled water at 85° C., be cooled, etc., as under (A) above.

Note: It is permissible to make up 2 liter instead of 1 liter solutions, dissolving by washing into flask with 1,800 cc. water at 85° C. in case of fluid extracts and 1,700 cc. water at 85° C. in case of solid or powdered extracts.

(8) *Total Solids:*

Thoroughly mix the solutions; pipette 100 cc. into tared dish, evaporate and dry as directed under "Evaporation and Drying." (See IV.)

(9) *Water:*

The water content is shown by the difference between 100 per cent. and the total solids.

(10) *Soluble Solids:*

S. & S. No. 590, 15 cm. single, pleated, filter paper shall be used for the filtration.

The kaolin used shall answer the following test: 2 grams kaolin digested with 200 cc. of distilled water at 20° C. for 1 hour shall not give more than 1 mg. of soluble solids per 100 cc., and shall be neutral to phenolphthalein. To 1 gram kaolin in a beaker add sufficient solution to fill the paper, stir and pour on paper. Return filtrate to paper when approximately 25 cc. has collected, repeating operation for one hour, being careful to transfer all kaolin to the paper. At the end of the hour remove solution from filter paper, disturbing the kaolin as little as possible. Bring so much as needed of the original solution to exactly 20° C. as described under (7), refill the paper with this solution and begin to collect the filtrate for evaporating and drying so soon as it comes CLEAR. The paper must be kept full and the temperature of the solution on the filter must not fall below 20° C. nor rise above 25° C. during this part of the filtration. The temperature of the solution used for refilling the paper must be kept uniformly at 20° C. and the funnels and receiving vessels must be kept covered.

Pipette 100 cc. of clear filtrate into tared dish; evaporate and dry as under (8).

(11) *Insolubles:*

The insoluble content is shown by the difference between the total solids and the soluble solids, and represents the matters insoluble in a solution of the concentration used under the temperature conditions prescribed.

(12) *Non-Tannins:*

The hide powder used for the non-tannin determination shall be of wooly texture, well delimed, and shall require between 12 and 13 cc. of N/10 NaOH to neutralize 10 grams of the absolutely dry powder.

(a) Digest the hide powder with 10 times its weight of distilled water till thoroughly soaked. Add 3 per cent. of chrome alum $(Cr_2SO_4)_3K_2SO_424H_2O$, in 3 per cent. solution, calculated on the weight of the air-dry powder. Agitate frequently for several hours and let stand over night. Squeeze and wash by digesting with four successive portions of distilled water, each portion equal in amount to 15 times the weight of the air-dry powder taken. Each digestion shall last for 15 minutes, and the hide powder shall be squeezed to approximately 75 per cent. water after each digestion except the last, a press being used if necessary. The wet hide powder used for the analysis shall contain as nearly as possible 73 per cent. of water, not less than 71 per cent. nor more than 74 per cent. Determine the moisture in the wet hide powder by drying approximately 20 grams. (See IV.) To such quantity of the wet hide as represents as closely as practicable 12½ grams (not less than 12.2 nor more than 12.8) of absolutely dry hide add 200 cc. of the original analysis solution and shake immediately for 10 minutes in some form of mechanical shaker. Squeeze immediately through linen, add 2 grams of kaolin (answering test described under (9)) to the detannized solution and filter through single folded filter (No. 1F Swedish recommended) of size sufficient to hold the entire filtrate, returning until clear. Pipette 100 cc. of filtrate into tared dish, evaporate and dry as in (8).

The weight of the non-tannin residue must be corrected for the dilution caused by the water contained in the wet hide powder.

Funnels and receiving vessels must be kept covered during

filtration. Flasks graduated to deliver 200 cc. are recommended for measuring the analysis solution to be detannized.

(b) Digest the hide powder with the amount of water and add the amount of chrome alum in solution directed under (a).

Agitate in some form of mechanical shaker for 1 hour and proceed immediately with washing and subsequent operations as directed under (a).

Note: In order to limit the amount of dried hide powder used, determine the moisture in the air-dry powder and calculate the quantity equal to 12½ grams of actual dry hide powder. Take any multiple of this quantity according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing as nearly as possible 73 per cent. of water. Weigh the whole amount and divide by the multiple of the 12½ grams of actual dry hide powder taken to obtain the weight of wet hide powder for 200 cc. of solution.

(13) *Tannin:*

The tannin content is shown by the difference between the soluble solids and the corrected non-tannins, and represents the matters absorbable by hide under the conditions of the prescribed methods.

III. ANALYSIS OF LIQUORS.

(14) *Dilution:*

Liquors shall be diluted for analysis with water at room temperature so as to give as nearly as possible 0.7 gram solids per 100 cc. of solution. Should a liquor be of such character as not to give a proper solution with water of room temperature it is permissible to dilute with water at 80° C. and cool rapidly as described under (7, A, a).

(15) *Total Solids:*

To be determined as in Extract Analysis.

(16) *Soluble Solids:*

To be determined as in Extract Analysis.

(17) *Insolubles:*

Determined as in Extract Analysis.

(18) *Non-Tannins:*

To be determined by shaking 200 cc. of solution with an amount of wet chromed hide powder, containing as nearly as possible 73 per cent. water, corresponding to an amount of dry hide powder shown in the following table:

Tannin range per 100 cc.	Dry powder per 200 cc.
0.35 —— 0.45 grms.	9 —— 11 grms.
0.25 —— 0.35 grms.	6.5 —— 9 grms.
0.15 —— 0.25 grms.	4 —— 6.5 grms.
0.00 —— 0.15 grms.	0 —— 4 grms.

Solutions to be shaken for non-tannins as in Extract Analysis and 100 cc. evaporated as in Extract Analysis.

IV. TEMPERATURE, EVAPORATION AND DRYING, DISHES.

(19) *Temperature:*

The temperature of the several portions of each solution pipetted for evaporating and drying, that is, the total solids, soluble solids and non-tannins must be identical at the time of pipetting.

(20) *Evaporation:*

All evaporations and dryings shall be conducted in the form of apparatus known as the "Combined Evaporator and Dryer" at a temperature not less than 98° C. The time for evaporation and drying shall be 16 hours.

(21) *Dishes:*

The dishes used for evaporation and drying of all residues shall be flat-bottomed glass dishes of not less than 2¾ inches diameter nor more than 3 inches in diameter.

V. DETERMINATION OF TOTAL ACIDITY OF LIQUORS.

(17) *Reagents:*

(a) One per cent. solution of gelatine neutral to hematine. The addition of 25 cc. of 95 per cent. alcohol per liter is recommended to prevent frothing. If the gelatine solution is alkaline, neutralize with tenth normal acetic acid and if acid neutralize with tenth normal sodium hydroxide.

(b) Hematine. A solution made by digesting hematine in cold neutral 95 per cent. alcohol in the proportion of ½ gram of the former to 100 cc. of the latter.

(c) Acid washed kaolin free from soluble matters.

(d) Tenth normal sodium hydroxide.

Directions:

To 25 cc. of liquor in a cylinder that can be stoppered, add 50 cc. of gelatine solution, dilute with water to 250 cc., add 15 grams of kaolin and shake vigorously. Allow to settle for at least 15 minutes, remove 30 cc. of the supernatant solution, dilute with 50 cc. of water and titrate with tenth normal soda using hematine solution as the indicator. Each cc. tenth normal soda is equivalent to 0.2 per cent. acid as acetic.

On public analytical work by members of this Association, the fact that the Official Method has been used, shall be so stated.

OFFICIAL METHODS FOR SAMPLING TANNING MATERIALS.

General:

Extract whether liquid or solid, and tanning materials in general all contain moisture. The amount of moisture varies with climatic conditions, but especially in liquid, and in most solid extracts becomes less as the extract is exposed to the air. As the value of any material shown by analysis is directly dependent upon the amount of moisture contained, and as an exposure of a comparatively few moments may alter appreciably the amount of moisture it is apparent that the sampling in all its details should be done as quickly as consistent with thoroughness and with great care to expose the material as little as possible to the air. The portions taken as samples should be placed at once in containers as nearly air tight as possible and preferably of glass. Wood, cardboard, poorly glazed crockery, etc., are all porous and more or less absorbent and not suitable for retaining samples.

Liquid extract cannot be accurately sampled when it contains any frozen material. A sample of extract taken after live steam has been run into the extract has not the same concentration as the original extract. A sample of spent bark which has been

standing where dust from fresh ground bark has sifted into it does not represent the degree of extraction of the spent bark. Samples of liquor which have stood with no preservative in them for some time do not represent the condition of the liquor when sampled.

(1) *Number of Packages to be Sampled:*

When carload lots, or less, of bags are to be sampled, 7 per cent. of the number of bags shall be sampled. When shipments of more than a carload and less than 2,000 bags are to be sampled, 20 bags shall be sampled. When shipments of more than 2,000 bags are to be sampled, 1 per cent. of the number of bags shall be sampled.

When 70, or less, barrels are to be sampled, 10 per cent. of the number of barrels shall be sampled. When from 71 to 140 barrels are to be sampled, 9 per cent. of the number of barrels shall be sampled. When from 141 to 210 barrels are to be sampled, 8 per cent. of the number of barrels shall be sampled. When from 211 to 280 barrels are to be sampled, 7 per cent. of the number of barrels shall be sampled. When from 281 to 350 barrels are to be sampled, 6 per cent. of the number of barrels shall be sampled. When from 351 to 420 barrels are to be sampled, 5 per cent. of the number of barrels shall be sampled. When 421 to 500 barrels are to be sampled, 4 per cent. of the the number of barrels shall be sampled. When more than 500 barrels are to be sampled, 3 per cent. of the number of barrels shall be sampled.

(2) *Liquid Extract in Barrels:*

The heads shall be removed from the number of barrels specified in (1), the contents of each barrel stirred until homogeneous, and a sample of equal size taken from each barrel. These sub-samples shall be put together in a suitable closed container and be thoroughly mixed. From this bulk duplicate samples shall be drawn for analysis. These samples shall be preserved in air-tight glass containers, labeled with the date of sampling and such distinguishing marks as may be necessary. When a considerable period of time is likely to elapse between

the sampling and the analysis, each individual sample shall be weighed when prepared and the certified weight of the sample be marked on the label.

(3) *Liquid Extract in Bulk:*

The extract shall be agitated with air, be plunged or be mixed by some other efficient means until homogeneous. Equal samples shall then be taken from different parts of the bulk, be placed in a proper container, be thoroughly mixed and sampled as described in (2).

(4) *Liquid Extract in Tank Cars:*

The following methods are permissible:

(a) The extract shall be unloaded into clean, dry containers and sampled according to (3); or,

(b) The extract shall be mixed until homogeneous, by plunging through the dome or other effective means, then numerous equal samples shall be taken from as widely scattered parts of the bulk as possible. These samples shall then be placed in a suitable container, be mixed and sampled as in (2).

Note: As it is almost impossible to secure a homogeneous mixture of the extract in a tank car, this method should be used only when no other is possible. Or,

(c) The extract shall be sampled as follows while the car is being unloaded:—A quart sample shall be taken from the discharge 3 minutes after the extract has begun to run; another quart sample shall be taken 3 minutes before the extract has all run out, and three other quart samples shall be taken at equal intervals between these two. These five samples shall be transferred to a suitable container as soon as taken, be thoroughly mixed and sampled as in (2).

(5) *Solid Extracts:*

The number of packages specified in (1) shall be selected, as nearly as practicable, of equal size. Whenever possible every nth package shall be set aside for sampling while the extract is being unloaded. When this is not possible, the packages shall be selected from as uniformly distributed parts of the bulk as possible.

Samples of as nearly equal size as practicable shall be taken from each package and these samples shall represent as nearly as may be, proportionately the outer and inner portions of the extract. These sub-samples shall be placed in a clean, dry closed container. When sampling is completed, the whole composite sample shall be broken up till it will pass through a sieve of 1 inch mesh; it shall be reduced to the required bulk by successive mixings and quarterings. From this bulk duplicate samples of the required size shall be taken, be wrapped in paraffine paper, and be enclosed in the smallest clean, dry air-tight glass receptacles that will hold them, labeled, etc., as in (2).

Sampling at place of manufacture shall be conducted by running a portion from the middle of each strike into a mold holding at least two pounds. These sub-samples shall be preserved with proper precautions against evaporation, and be sampled for analysis as above.

(6) *Crude Tanning Materials:*

A. Shipments in bags, mats, barrels or other similar packages.

The number of packages specified in (1) shall be emptied in uniform horizontal layers in a pile on some clean surface. At least five equal samples shall be taken from top to bottom through the pile at uniformly distributed spots. These sub-samples shall be mixed together and the bulk be reduced by mixing and quartering to the desired size. Duplicate samples of not less than two quarts each shall be preserved in air-tight containers properly labeled.

When the number of packages to be sampled is so great as to make one pile impracticable, two or more piles may be made, and the samples from the several piles properly mixed.

B. Shipments in bulk.

1. Nuts, beans, pods, ground materials, etc.

Equal portions shall be taken from at least ten uniformly distributed parts of the bulk, be mixed and sampled as in "A."

2. Bark, wood, etc., in sticks.

Sticks shall be taken from at least ten uniformly distributed parts of the bulk, be sawed completely through, and the sawdust thoroughly mixed and sampled as in "A."

C. Materials prepared for leaching.

Samples of equal size shall be taken at uniform intervals as the material enters the leach and be kept in a suitable container till sampling is completed. This bulk shall then be thoroughly mixed, be reduced by mixing and quartering, and duplicate samples for analysis of at least one quart in size be preserved in air-tight containers, as in "A."

(7) *Spent Material from Leaches:*

Samples of spent material shall be taken from the top, middle and bottom, and in each case from the center and outer portions of the leach. These sub-samples shall be thoroughly mixed, be reduced in bulk by mixing and quartering, and duplicate samples of at least one quart in size be preserved for analysis.

(8) *Tanning Liquors:*

The liquor shall be mixed by plunging or other effective means till homogeneous and then samples of at least one pint be taken for analysis. The addition of 0.03 per cent. of thymol or other suitable anti-ferment to the sample is essential to keep the liquor from altering its original condition.

When routine samples are taken from day to day and a composite sample analyzed, samples of equal size shall be taken from each vat after thorough mixing, be preserved in covered containers in as cool a place as possible, and be kept from fermentation by the addition of suitable anti-ferment, as above. This bulk shall be mixed till homogeneous and samples of not less than one pint each be preserved for analysis.

When a sample is taken by a member of this Association in accordance with the above method, it is requested that he state both upon the label of the sample submitted and upon the analysis blank that "this sample has been taken in accordance with the official method of sampling of The American Leather Chemists Association."

OFFICIAL METHOD FOR LEATHER ANALYSIS.

(1) *Preparation of Sample:*

The sample of leather for analysis shall be reduced to as fine a state of division as practicable, either by cutting or grinding.

(2) *Moisture:*

Dry 10 grams of leather for 16 hours at a temperature between 95°-100° C.

(3) *Fats:*

Extract 5 to 10 grams of air-dry leather in a Soxhlet apparatus until free from grease, using petroleum ether boiling below 80° C. Evaporate off the ether and dry to approximately constant weight.

Or, if preferred, extract 30 grams of leather as described above. In the latter case, the extracted leather, when freed of solvent, may be used for the determination of water-soluble material.

(4) *Ash:*

Incinerate 10 to 15 grams of leather in a tared dish at a dull red heat until carbon is consumed. If it is difficult to burn off all the carbon, treat the ash with hot water, filter through an ashless filter, ignite filter and residue. Add the filtrate, evaporate to dryness and ignite.

(5) *Water-Soluble Material:*

Digest 30 grams of leather in a percolator over night, then extract with water at 50° C. for three hours. The total volume of solution to be 2 liters. Determine total solids and non-tannins according to the Official Method for extract analysis.

(6) *Glucose:*

To 500 cc. of the solution obtained by extraction according to (5), add 20 cc. of normal lead acetate, shake well, let stand for an hour and filter. To 400 cc. of filtrate add dry Na_2CO_3 and filter. To the filtrate add 5 cc. concentrated HCl and boil for two hours, allowing the solution to evaporate to about 90 cc. Add dry Na_2CO_3 until the solution is about neutral, make up to 100 cc. and filter if necessary.

Take an aliquot part containing not more than 0.25 gram of sugars, add to 60 cc. of Allihn's Fehling's solution, dilute with water to 145 cc. if necessary, cover with a watch-glass, bring to boil and set in a boiling water-bath for exactly 30 minutes. Filter

through an asbestos mat in Gooch crucible, wash with hot water to free from soluble salts and finally with alcohol, dry 1 hour in water oven, cool and weigh. Multiply the weight of cuprous oxide by 0.8883 and calculate to glucose according to the table of Koch and Ruhsam. (See *J. S. C. I.*, XIII, 1227, etc.; also this J., IV, 125, etc.; also pamphlet of *Methods of A. L. C. A.*)

(7) *Nitrogen:*

Gunning modification of the Kjeldahl Method. *A. O. A. C. Bulletin*, No. 107 (1907).

Reagents.

Standard Acid Solutions.—Hydrochloric or sulphuric acid, the absolute strength of which has been accurately determined. For ordinary work half-normal acid is recommended. For work in determining very small amounts of nitrogen, tenth-normal is recommended. In titrating mineral acid against hydroxide solution use cochineal as indicator.

Standard Alkali Solution.—The strength of this solution relative to the acid must be accurately determined; tenth-normal solution is recommended.

Sulphuric Acid.—The sulphuric acid used should have a specific gravity of 1.84 and be free from nitrates and also from ammonium sulphate.

Sodium Hydroxide Solution.—A saturated solution of sodium hydroxide free from nitrates.

Potassium Sulphate.—This reagent should be pulverized before using.

Indicator.—A solution of cochineal is prepared by digesting and frequently agitating 3 grams of pulverized cochineal in a mixture of 50 cc. of strong alcohol and 200 cc. of distilled water for a day or two at ordinary temperature; the filtered solution is employed as indicator.

Determination.

Place 0.7 gram leather in a digestion flask. Add 10 grams powdered potassium sulphate and from 15 to 25 cc. (ordinarily about 20 cc.) of concentrated sulphuric acid. Place the flask in an inclined position and heat below the boiling point of the acid

from 5 to 15 minutes or until frothing has ceased (a small piece of paraffine may be added to prevent extreme foaming).

Then raise the heat and boil briskly until the liquid has become quite clear and nearly colorless (the digestion should take from 4 to 5 hours).

After cooling, dilute with about 200 cc. of water. Next add 50 cc. soda solution, or sufficient to make the reaction strongly alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distill until all ammonia has passed over into the standard acid. The first 150 cc. will generally contain all the ammonia. The operation usually requires from 40 minutes to 1 hour and a half. The distillate is then titrated with standard alkali.

Previous to use, the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates present that otherwise might escape notice.

INQUIRY INTO ELECTRICAL TANNAGE.*

PRELIMINARY NOTE.

By O. J. Williams, Bristol University.

The phenomenon of electric endosmose, or the property of the electric current by which it mechanically carries part of certain liquids through porous partitions, and especially the electric endosmose of tannic acid solutions through hides, are matters of considerable importance to the tanner. The principle of relative motion of hide and liquor (e. g. drum tannage) has been adopted with some success in the tanning industry, for hastening the process of tanning, but electrical tannage has been a failure.

In this inquiry I tried to trace the reason or reasons of the failure of electrical tannage.

The phenomenon is very considerable with tannic acid solutions through hides. Roever[1] found that an E. M. F. of 100

* *Collegium*, March, 1913, 76-8.

[1] "The Electric Endosmose of Tannic Acid Solutions through Hide Diaphragms", by F. Roever. Wiedemann's *Annalen*, Vol. 57, No. 2, p. 397.

volts from a battery of accumulators would force 7.377 kilograms of tan liquor through 1 sq. m. area of hide per hour. The hide was in the condition in which it is found in the tannery and the tannic acid solution used was a 0.2 per cent. solution of quebracho extract in clean water. It was found also by the same investigator, that the weight of tan liquor forced through the hide by the electric current was almost independent of the direction of the current, and "in order to promote the circulation of the tan liquor in the pores of the hide" he suggests that the electric current should be reversed at short intervals of "say every minute."

It may be seen from the above given facts from the work of Roever that the failure of electrical tannage is not due to the hide preventing the passage of the tan-containing solution, and it was hence thought possible that the electric current destroys the tannins and converts them into non-tannins, and that the failure is due to this cause.

Such a conversion of tannin into non-tannins of tannic acid is in full agreement with Nierenstein's view, who regards tannic acid[2] to be a polydigalloyl leucodigallic-acid-anhydride, which would thus be decomposed by the electric current into gallic acid, which is a non-tannin.

This spells failure to electrical tannage by direct current electricity. The transformation of tannic acid into non-tannins was investigated in the following way:

1. Observations were taken of the changes in the optical activity produced by electrolysing the solution.

2. Estimations were made of the non-tannins formed (the non-tannins were estimated according to Körner and Nierenstein).[3]

I. CHANGES IN THE OPTICAL ACTIVITY OF TANNIC ACID CAUSED BY DIRECT CURRENT ELECTRICITY.

A preliminary inquiry showed that the optical activity of an

[2] M. Nierenstein, *Annalen der Chemie*, **388**, 223 (1912), and *Collegium*, 1912, p. 197.

[3] Nierenstein, *Chemiker-Zeitung*, **36**, 31 (1911), and *Collegium*, 1911, p. 80.

aqueous solution of tannic acid is decreased by the passage of a direct electric current.

For comparison I also give the following table shownig the rate at which the optical activity changes with age of solution. It will be seen that it decreases but slowly.

FIVE PER CENT. SOLUTION OF TANNIC ACID IN TAP WATER.

Age of solution days	0	1	3	6	17	29
Optical activity $[\alpha]_D^{17° C.}$	55.0°	54.8°	54.2°	54.0°	53.6°	53.0° [4]

The solution was kept in a stoppered bottle at even temperature 15° C. A fresh 5 per cent. aq. solution of "pure" tannic acid gave = 56.6 was decreased to 51.2 by the passage of direct current through it for half an hour at 17° C. between carbon plates 58.2 sq. cm. effective area, immersed in the liquor. The current density was of the same order as the current densities used by Roever, being about 0.004 amp. per sq. cm. As will be seen, the direct electric current decreases the optical activity.

2. EFFECTS OF DIRECT AND ALTERNATING ELECTRIC CURRENTS ON TANNIC ACID. THE TRANSFORMATION OF TAN INTO NON-TAN BY MEANS OF DIRECT CURRENT.

For this purpose I used a conductivity cell (platinum plates, but not platinised), and the following current densities: — 0.075, 0.050, and less than 0.02 ampere per sq. cm. First direct current and then alternating current at 93 periods per second (town supply).

The following are results with 5 per cent. solutions of pure tannic acid in distilled water at 16 C.:

Solution No.	Electric current direct or alternating	Current density amperes per sq. cm.	Duration of electrification minutes	Percentage of non-tan Before electrification	Percentage of non-tan After electrification
1	Direct	Less than 0.02	15	4.86	34.22
2	Alternating	Same as for No. 1	15	4.86	5.22
3	Alternating	0.050	15	4.86	5.02
4	Alternating	0.075	15	4.86	5.48
5	Direct	Less than 0.02	30	4.86	47.12
6	Alternating	0.050	30	4.86	5.26

[4] Strong coloration with KCN solution due to the formation of gallic acid.

CONCLUSIONS.

1. The passage of a direct current of electricity rapidly destroys the tan in tan liquor (probably in the same way as it eventually becomes destroyed by high temperature or by aging).

2. Alternating current of 93 periods per second has hardly any effect on the tan in the liquor, but nevertheless it will accelerate the tannage of hides by electric endosmose.

It seems to follow that chemical tannage associated with chemical E. M. F.'s (and therefore unidirectional currents) can never be a success, and the only satisfactory way to accelerate tannage is by means of alternating electric currents.

SOME EXPERIMENTS ON THE THEORY OF ELECTRO-TANNING.*

By Dr. E. K. Rideal and U. R. Evans.

It has for some time been known that the diffusion of tanning substances into hides—a process which is usually rather slow—could be accelerated considerably by causing a current of electricity to flow through the liquid in which the hides are being tanned. Many attempts have been made to utilize this fact in "quick tanning processes."

The first use of "galvanism for tanning purposes" was made as early as 1849 by Crosse, who placed electrodes of zinc and lead in an ordinary tanpit. Rebu in 1861 made further experiments, and de Mertass of St. Petersburg in 1874 designed an electric-tannage process, which continued to be used in nearly 600 pits for some years. Processes for electrical tanning were also worked by Nielson) of Norrköping, Sweden) about 1889, and by Worms and Bale in France in 1887. The latter (*J. S. C. I.*, 1888, p. 443) used the combination of "electricity and motion."

About 1888 Groth invented his method of electrical tanning; in this process, also, the hides were kept in motion during the electrical treatment; Rideal and Trotter (*J. S. C. I.*, 1891, p.

**J. S. C. I.*, XXXII. 633-8, June 30, 1913.

425), who examined the process scientifically, found that the acceleration was largely due to the electricity, although partly due to the motion.

But all these processes have been, on the whole, empirical, and very little work has been done to ascertain the exact nature of the forces in action and of the influence of external conditions. Such an investigation, however, must be introductory to an attempt to settle the best conditions under which good leather can be produced both quickly and cheaply. And, until such experiments have been made, it is not possible to condemn electrotannage merely because certain leathers of inferior quality—said to have been "electrically tanned"—have come on to the market.

In the following experiments some attempt has been made to find the nature of the transference of tannin by the electric current, and how it is affected by external circumstances. Some inquiry has also been made as to the chemical changes which occur in tannic acid on its electrolysis. In this way it has been possible to outline the conditions which will ensure quick transfer of the tan-substance through the hide, at a low expenditure of electrical energy and tan material.

Theoretical:

A. Modes of Transfer. Three modes of transfer of matter in liquids are known to be possible under the influence of an electric current; these are (1) ionic conduction, which involves the passage of dissolved matter (as ions) in both directions, and also chemical decomposition at the electrodes.

(2) Cataphoresis, which involves the movement of "colloid" particles, apparently, as a rule, in one direction only and without perceptible decomposition.

(3) Electric endosmose, or bodily transfer of a liquid or solution (including the solvent) through a porous wall.

There is no reason why tannic acid solutions should not show all these three modes of transfer.

B. The effect of additions has to be considered since organic acids are in practice formed in the tan-bath as the result of fermentation, and since it has been proposed to add various salts to electrical tan baths. The addition of electrolytes will

(1) greatly alter the concentration of the ions of tannic acid;

(2) often alter the velocity, and sometimes the direction, of the cataphoretic movement;

(3) decrease the endosmotic movement.

But the two most important effects have still to be stated:—

(4) Such additions will greatly increase the conductivity of the solution as a whole. Thus, if an electrolyte be added to a tannin solution, even if the number and mobility of tannin-ions be not reduced, the total conductivity of the solution will be so much increased by the addition of the electrolyte, that the proportion of the current used in the useful work of tannin transference is reduced to a small fraction.

(5) The full "back E.M.F. of polarization" at the electrodes is arrived at more quickly and maintained more completely if the solution as a whole has a high conductivity.

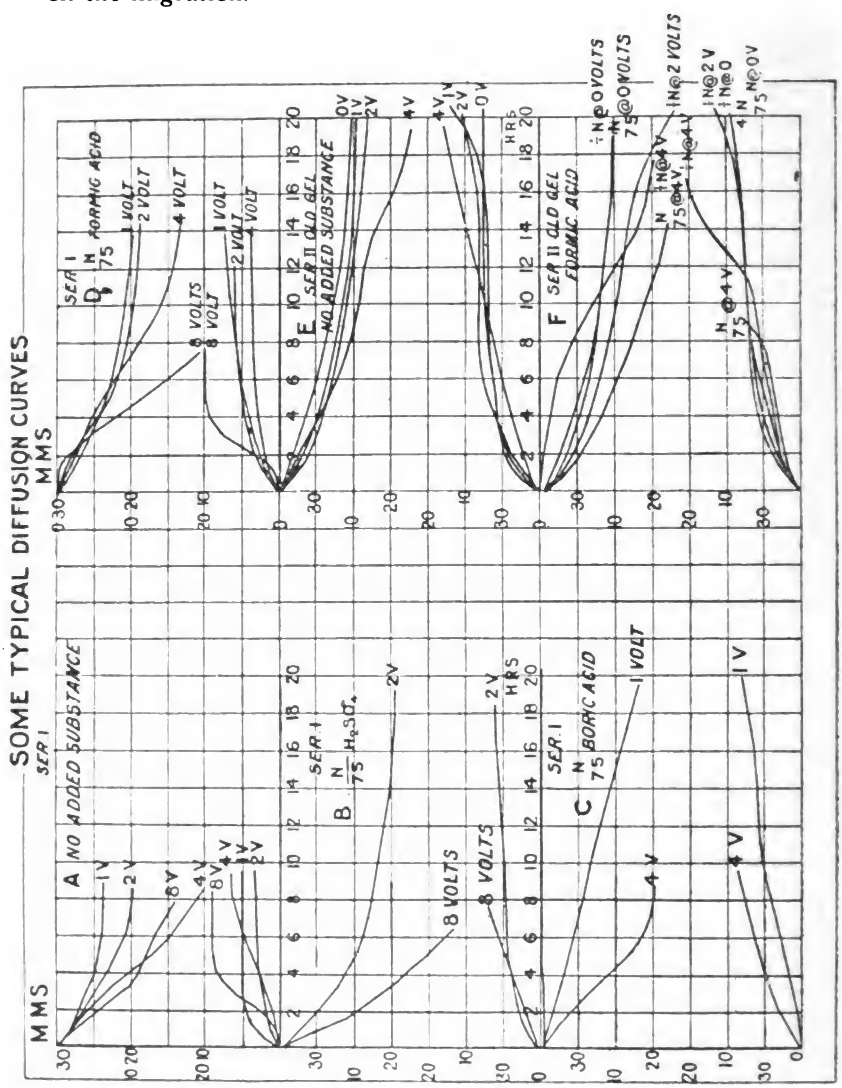
C. The nature of the electrode material will have a large influence upon the amount of electrodic decomposition of the tanning-matter. This is of the utmost importance, both with a view to avoiding loss of tannin, and also because the products of decomposition are often electrolytes and produce the undesirable effects that have been described.

Experimental:

Two classes of experiments were performed. Firstly, experiments were made in cells divided by porous partitions in order to investigate separately the effect of electrodic decomposition at the two poles, and also to note the influence of the electrodic material on this decomposition. At the same time, the phenomenon of eletric endosmose was observed and its amount measured.

But for the purpose of examining the migration of tannin through a substance, a porous pot was clearly unsuitable. The greater portion of the work was therefore devoted to tracing the progression of tannin under the influence of an electric current, through narrow tubes filled with gelatine jelly. This jelly contained a trace of ferric chloride, and as the tannin penetrated into it, the coloration (due to the so-called "ferric tannate") was produced, and forms a means of observing its advance quantitatively. In most experiments, additions were made to

the tannin solution, for the purpose of ascertaining their effect on the migration.



I. "Divided cell experiments."

It is impossible to describe in detail the various experiments made in porous pots. The general method of procedure was as

follows: A round porous pot containing one electrode was placed in a glass jar containing the other electrode; measured volumes of liquid were poured into the two compartments, and a known E.M.F. (usually 4 volts) was applied for several hours; the current passing was measured on an ammeter and the temperature, etc., was noted in each case. The liquid used was generally tannic acid solution in both compartments, but in some cases the outer solution contained only dilute potassium chloride; to test the influence of additions to the tannin liquor, salts were in some experiments added in varying proportion to the tannic acid solution. The conductivity of the solution in both cells was measured before and after the experiment, and in some cases the "acidity" was also determined by the electrometric method of Sand, Wood and Law. (This J., 1911, pp. 114 and 428.) These numbers gave a clue to the amount of decomposition that was caused at the electrodes, the electrodic material being also varied in different experiments. The volume of liquid in the two compartments was noted after the experiment, and thus the rate of endosmose could be arrived at.

The details of two experiments may be given as an example. They are shown for comparison in parallel columns:—

	Experiment A	Experiment B
Electrolyte in both compartments	1 per cent tannic acid	1 per cent. tannic acid
Electrode material	Carbon	Copper
Electrode area	5½ square inches	5½ square inches
Temperature	18°	18°
E. M. F. applied	4 volts	4 volts
Current amperes	0.004 sinking to 0.001	0.002 sinking to 0.001
Specific resistance, of solution used, before electrolysis, per cm. cube	7,481	10,660
Specific resistance, after experiment, in cathode compartment, per cm. cube	6,454	2,000
Specific resistance, after experiment, in anode compartment, per cm. cube	567	3,258

Similar results were obtained with 4 per cent. tannic acid.

Although no two experiments with porous pots can be exactly comparable, the general conclusions arrived at were clear:—

(1) A copper cathode causes more cathodic decomposition to a tannic acid solution than a carbon cathode; but a copper anode brings about less anodic decomposition than a carbon anode. This is to be expected.

(2) The addition of salts such as potassium sulphate does not interfere seriously with the rate of endosmose at constant E.M.F. But they reduce the amount of tannin matter which takes part in the endosmose. Thus a pure tannin solution moving through a porous pot carries its tannin with it, but, in the presence of potassium sulphate, the solvent "leaves the tannin behind."

(3) The endosmose takes place in the "positive to negative" direction.

II. "Jelly Tube" Experiments.

A jelly consisting of 5 per cent. Nelson No. 2 gelatine, dissolved in water containing 0.1 per cent. of ferric chloride (a strength which produces a good coloration with tannin) was introduced into a series of glass tubes (Fig. 1). These glass tubes are 10 cms. long and of 0.2 cms. internal bore; they contain a length of about 3.6 cms. of the jelly situate at about 2 cms. from the top end. The bottom of each tube was placed in a small test-tube (0.6 cms. diam.) and was filled up to the gelatine with a 4 per cent. solution of tannic acid. The space above the gelatine (and also the test-tubes) was similarly filled with the same solution. T. By means of copper wires C, C[1] connected to mercury troughs any number of these tubes could be connected to sources of current at different E.M.F.'s. The wires at the bottom formed the positive electrodes, and those above the negative electrodes.

A series of such tubes were arranged vertically, attached to a thin board behind. By means of a strip of squared paper placed as a scale behind the row of gelatine containing tubes, the advance of the coloration produced by the interaction of the migrating tannin with the ferric chloride solution could easily be followed. Readings of this advance from both ends were taken

over a period of about 30 hours. In some tubes pure tannic acid solution was used, in others small quantities of substances, whose influence we were anxious to investigate, were added to the solution at both ends of the tubes. The E.M.F. applied was varied in the case of different tubes; in the second series of experiments, a number of blank experiments were made in which no

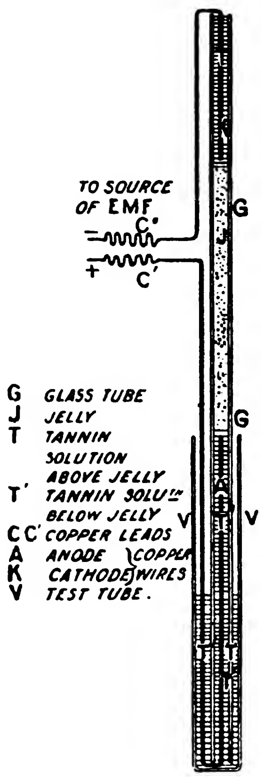


Fig 1.

E.M.F. was applied, with a view to obtaining separately the transfer due to natural diffusion. In this second series of experiments the concentration of the substance added was varied, while in the third the strength of tannic acid solution employed is also changed. The "age" of the jelly also differs in the three series of experiments, *i.e.*, the gelatine has been permeated for a different time with the ferric chloride.

In every case the tannin was observed to enter the tube in *both* directions. The most important migration is in the negative to positive direction, and is apparently due to *ionic or cataphoretic* movement. The less rapid entry of the tannin—in the positive to negative sense—is presumably due to the *endosmose* observed in the porous pot experiments; this view is confirmed by the form of the boundary of advance, which supports the view that the solvent as a whole is penetrating the jelly, and taking advantage of any flaws occurring therein. (Fig 2.) The advance in the opposite direction shows a smooth front.

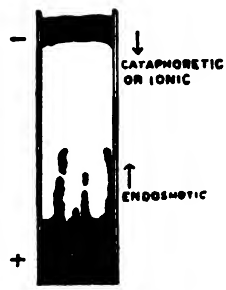


Fig 2.

Curves were plotted to show the gradual movement of the tannin into the jelly in both directions. A few of these curves are shown as examples. The abscissæ represent the time in hours, the ordinates the position on the tubes. (See p. 334.)

A............	New jelly	No added substance
B............	New jelly	N/75 H_2SO_4
C............	New jelly	N/75 Boric acid .
D............	New jelly	N/75 Formic acid
E............	Older jelly	No addition
F............	Older jelly	Formic acid, various strengths

A few of the experiments made in the first series had to be repeated, notably those in which potash, sodium acetate and phenol respectively were added to the tannin solution, since it became evident that the coloration the advance of which had been followed was not due to the formation of ferric tannate, but to ferric hydroxide, acetate and phenate respectively. A few other apparently anomalous results obtained in the first series were subsequently explained.

It was observed that the older the jelly, the slower was the diffusion; this was due to the hardening action of the ferric salt.

Discussing the form of the "negative to positive" movement (ionic or cataphoretic) as shown by the downward curves, we see that

(1) The greater the potential gradient, the quicker the transference, in general;

(2) On the whole, additions to the tannic acid, in concentrations between N and N/75 have very little effect upon the rate migration of tannin at constant voltage. In one or two cases, *e.g.*, in presence of N/75 formic acid at 4 volts in old jelly, the addition seems to cause a slight acceleration to the transfer; but this is not enough to compensate for the disadvantages caused by such additions.

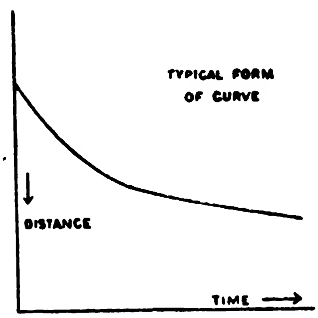


Fig. 3.

(3) The curves tend to approximate to a certain typical form (Fig. 3) in which the gradient falls off at first with the time, finally becoming constant. This is due to two causes:—

a. Natural diffusion at first aids the migration.

β. There is a tendency for polarization to occur. Thus this "typical form" of curve becomes all the more marked when strong electrolytes are substituted for weak ones.

The upward curves show the "positive to negative" (endosmotic) movement.

(1) This is much less rapid than the "negative to positive" migration, being comparable to the rate of natural diffusion.

(2) It is less dependent on the applied E.M.F.

(3) In the presence of comparatively large quantities of such electrolytes as potassium sulphate, sulphuric acid and formic acid, at the lower voltages, tannin does not seem to take part in the endosmose.

Strong tannic acid solutions show a more rapid diffusion (in both directions) than weak ones.

The main conclusions to be drawn from the experiments are as follows:—

(1) Ionic or cataphoretic migration is the main agency involved in the transference of tannin through gelatinous substances and *not* endosmose (which causes a less rapid transfer in the opposite direction).

(2) The addition of acids and metallic salts decrease the transfer per kilowatt hour because

A. They cause conduction of current in a way which does not involve the transfer of tannin.

B. They cause polarization at an unduly early stage, and so reduce the effective E.M.F.

C. They reduce or inhibit the tannin carried by endosmose. especially at high concentrations.

D. Some have a specific slowing action upon the ionic migration.

Incidentally in their presence, when attackable anodes (*e.g.*, of copper) are used, these suffer an undue electro-chemical attack.

(3) If we assume that the jelly offers an approximate analogy to the structure of a hide substance it is clear that, in the absence of acids and conducting salts, a very small expenditure of electrical energy can cause a great increase in the rapidity of the transference of tannin through a hide—which is probably the slowest part of the tannin process.

(4) The electrode material has an important influence on the success of an electro-tanning process, because if an unsuitable material be used, an undue decomposition will occur at the electrodes, and so (A) tanning matter will be destroyed (B) acids will be produced, which will produce the undesirable effects outlined above.

For this reason it is best to use *cathodes of carbon and anodes of copper,* and to keep the bath sterile; in this way, an undue wastage of energy and tannin is avoided. But for some purposes the tanner insists upon a bath containing relatively large amounts of organic acids (which *may* be necessary for the reaction between the tannin matter with the hide substance, *after* it has penetrated into the latter); in such a case, it would be extravagant to use copper anodes, which would be quickly attacked in the highly conductive solutions, and carbon anodes also may be employed. But so far as possible, every endeavor should be made to keep the total conductivity of the tan bath as *low* as possible.

It must, of course, be remembered that the transference of tannin into the hide substance is not the only part of the tanning process, although it is doubtless the slowest and most satisfactory. But, after the tanning substances have entered the hide, there is doubtless some sort of chemical reaction between them and the hide material, and it is for the tanning chemist to settle the conditions most favorable to this combination. Possibly these may not be the conditions which are most suitable for the economical electro-chemical transference of the tannin through the hide; but if the electro-chemist clearly states what conditions are most favorable to *his* part of the process, and the tanning chemist will tell us within what limits the chemical interaction will proceed satisfactorily, doubtless some compromise could be arrived at, which would result in a successful tanning process. (For instance, the electro-chemist will desire as low a bath acidity as possible; the tanning chemist may—for some purposes—prefer a high one; but there may be some intermediate strength which would suit both.)

It may be suggested as a possibility that endosmose—which involves the bodily transfer of the solution through the hide—may prove a destructive form of introduction of tanning matter into the latter; for, as was observed in the case of the jelly-tube experiments, advantage will be taken of any points of weakness in choosing its path, and this weakness will, therefore, probably be increased. If this is so, it may well be advantageous to avoid endosmose as much as possible, and it is satisfactory to find that

it is not the main agency of transport involved in electro-tannage. The fact that the entry of the tannin is dissimilar in the two directions, as well as the fact that hides are themselves dissimilar on the two sides, must be taken into account in the settlement of the relative times during which the current should pass in the two directions.

Within the last few months, O. J. Williams has published a research upon the subject of electro-tannage. The figures which he quotes have little bearing on the matter since he assumes electric endosmose to be the only agency at work. But he is right in regarding the loss of tannin matter by electrodic decomposition as one of the main problems to be dealt with in an electro-tanning process. He proposes the employment of an alternating current, which in his view should cause no decomposition, and yet allow the endosmose to proceed. But it is difficult to see how—unless a valve-like structure be assumed to exist in the hide—an alternating current of sufficiently high frequency to prevent electrodic decomposition could, *per se*, produce any endosmotic movement of tanning liquor through the hide. The best method of preventing the electrodic destruction of tannin is a careful choice of the material and form of the electrodes employed, and a scientific control of the composition of the bath.

DISCUSSION.

Mr. W. Colebrook Reynolds asked whether the movement of the iron of the indicator towards the cathode had been taken into account. If not, the apparent movement of the tannic acid would be partly illusory.

Dr. Parker said that 17 or 18 years ago he had gone over to Sweden to investigate the process of tanning assisted by electric current, and he was very much impressed with a demonstration of it in a large tannery at Wennersborg, Sweden, where they were tanning some 400 to 500 hides each week. The tanning process was apparently accelerated and the penetration of the tannin into the fibers of the hide was apparently assisted by the electrical current. During the past 18 years, however, great changes have taken place in the processes of leather manufacture. Years ago sole leather required twelve months to be properly

tanned. Nowadays that period had been reduced to as many weeks, and a good leather could even be tanned in as short a time as twelve days. Some years ago, in Vienna, a tanner, in order to win a bet, undertook to tan some leather and have it made into a pair of boots, all within forty-eight hours. An ox was slaughtered in the city abattoir at six o'clock in the morning. The hide was immediately conveyed to the tannery, tanned, dried and finished, and within forty-eight hours after the tanner appeared in the café wearing the finished boots. In this instance there was no record as to the quality of the leather. If leather could be made and turned into a pair of boots in forty-eight hours, any claim made on behalf of electrical acceleration fell rather flat. For some years he had initiated and carried out in his laboratory various tests connected with electrical tanning, and he had failed to produce a process which offered considerable commercial advantages. In other words, he had never been able to tan on a practical scale quicker or better by the aid of electrical current than he had been able to tan by various mechanical means with chemical assistance, added to which the latter were cheaper. Practical tanners did not worry so much about the quality of the leather as the cost of production. What was wanted to-day was that from a given weight of hide substance a given weight of finished leather should be produced at a certain cost per lb., and they were loath to adopt any process which, if it gave the same results, would add a fraction of a penny to the cost of production, even if the leathers produced by this means were slightly better. Thanks to Procter's work and to the work of other of their members, they had advanced very considerably in their knowledge of the chemistry both of the raw materials and of the process of leather manufacture during the last eighteen years. They now understood more fully the action of the acids and alkalis upon hides. They understood how to accelerate the penetration of the tan through the hide substance—so much so that really good leather could be turned out in the tanyard in fourteen days—therefore, the advantage of speed claimed by those who advocated the use of electricity was not now so important a matter as it was eighteen years ago. The authors, while they had not dealt with the subject from a practical stand-

point, had certainly given some theoretical points for consideration, and he was thinking how those theories which they had propounded might be carried out on a practical scale. If they would come to the Leathersellers' Technical College he would provide 20 or 40 hides, or as many as they wanted, and they could fit up their apparatus, and if they got any more weight than he could get, or if they could produce leather more quickly than he could, or better leather, and, last but not least, cheaper, they would have him for a convert at once. He would be prepared to take corresponding hides to them, using the same liquors but using drums or paddles, as the case might be. All that took place in the process of leather manufacture was not yet understood, but much information had been gained by the work of Procter and others in connection with colloidal chemistry, and the researches which had been carried out dealing with the effect of swelling and tanning of hides by means of acids and various salts in the liquors. He did not desire to convey the impression that he looked upon the use of electricity in connection with tanning to be hopeless, but he had tried it with weak currents, alternating and direct, and had tried it all ways, but he had now given it up. Another point, and one on which he bowed to the authors of the paper, was that he was not sure whether his process would conserve the tanning acid as much as they claimed to do. They did not give figures, but they pointed out that there was not the same decomposition of tannic acid by their process as by the ordinary processes, but he had been taught to believe that the decomposition of tannic acids, or rather the hydrolysis of tannin, produced beneficial acids, and the fermentation of the glucoses produced acids. Unless the early liquors were kept acid enough, that is to say, if one did not have a proper fermentation going on in the tanyard which could produce sufficient lactic, acetic and propionic acids, they would not get sufficient swelling. If the leather was not sufficiently swelled in the early processes of tanning they would neither get sufficient weight into the leather, nor would the leather be thick and solid, as it must be to possess good wearing qualities; and unless these acids were present there would not be the decomposition of semi-soluble substances inside the hide. It had been claimed as an advantage

that the electrical process kept the liquors sterile. He would be rather sorry for the tanner whose liquors were sterile, because, unless he had misunderstood the authors, he was afraid that if the liquors were kept sterile and there was no acidity present, the leather would be flat, tinny and brittle, and practically would not produce a commercial product.

Dr. E. RIDEAL, in reply, said it had been mentioned that the decomposition at the electrode varied, and it seemed to have been gathered from the paper that the rate of movement in the liquid itself varied with the nature of the electrodes used. That was not what they had intended to convey. What they had intended to say was, that, supposing they had a soluble anode, the decomposition was less than if they had an insoluble anode, because, instead of oxygen being liberated and attacking the tanning substance, the electrode itself went into solution and the tannic acid was left unchanged. The actual actions in the body of the electrolyte itself, the velocity of the tanning, and the rate of diffusion was not influenced very much by the electrodes. With reference to an iron chloride indicator, certainly iron travelled a certain rate with the current, but there was always sufficient iron to give a coloration; and the natural diffusion was also a check on it, because the same error ran through the whole of the results, which were strictly comparable.

With reference to the unsuccessful nature of the past experiments on practical electric tanning on a large scale, he thought a great deal could be attributed to the high conductivity of the bath itself. When they worked on a large scale they got little traces or possibly even large amounts of salts of lime, etc., which got in from the previous treatment undergone by the hides before they were ready for the tan bath; that affected the conductivity and thus permitted a great deal of current to go through which was not aiding the tanning, which in fact acted rather detrimentally to the tannic acid; for the greater current caused greater action at the electrodes themselves, which action decomposed the tannic acid and involved a great waste of tannic acid. If, however, the bath had to be acid, carbon electrodes should be used instead of copper ones. They did not intend to suggest that the liquor was kept sterile by means of electric current itself, but

they suggested it should be kept sterile by adding some suitable sterilizer, provided that the right quantity of acid which was demanded was kept there. Apparently in practice the baths might get very powerfully acid and the liquor become inefficient, or they might cease to be sufficiently acid. There ought to be some degree of acidity which is the correct acidity for hide treatment. Procter was not quite certain which was the correct acidity, but that should be experimentally arrived at.

DEVELOPMENT OF THE LEATHER INDUSTRIES DURING THE LAST FEW DECADES.*

Lecture by Dr. Edmund Stiasny at the Chemical Engineering and Industries Exhibition, London.

Tanning has developed along four lines; machines have replaced hand work in many processes, new tanning materials have been introduced, methods are more rapid and more economical, and the work as a whole is much better organized than formerly. The introduction of power might seem the most important factor in development, but further application of chemical knowledge will probably be the greatest help in the future. Time was when oak bark and sumac were practically the only vegetable tanning materials used, when alum was the only mineral and cod the only oil tannage known. To-day more than 20 vegetable tanning materials are in use, chrome tannage is widely practiced, and iron tannage seems to have reached the practical stage. Combinations of chrome and alum tannages and of chrome with vegetable tannins have their distinct uses. Formaldehyde and quinine each produce a white leather which withstands the boiling temperature. The time of tannage has been much reduced. In the 18th century, liming extended through a whole year, and tannage through two more.

Development in the future will in all probability be more rapid than in the past. Science has but just begun to influence the industry. The I. A. L. T. C. started in 1897 with 15 members, and to-day has more than 500. The number of manu-

* Condensed from the report in *Leather Trades Review*, July 2, 1913.

facturers employing chemists is rapidly increasing, and the fate of those who prefer to continue rule of thumb methods may be easily foretold.

Knowledge of the scientific principles involved in leather manufacture is rapidly growing. Little is known as yet in regard to the chemical changes in the hide due to the processes of liming, bating and pickling. What it will mean to have light penetrate this darkness no one can fully imagine. In the process of liming, the lime or the alkaline sulphide is used with the object of dissolving some proteins of the hide without attacking some of the others, to swell the fibers, to separate them, to saponify the natural fats, etc. The action in the limes is partly chemical and partly bacteriological. What we aim at is to get the hair loosening, swelling and plumping effect with no loss of valuable hide substance. Present methods are no doubt open to much improvement, and the same is the case with methods of controlling the liming process. The total amount of nitrogen present in an old lime tells nothing definite. So long as we are unable to distinguish between the nitrogen of different origins, say between the nitrogen derived from collagen and that from the leucine, keratin, etc., we cannot judge if valuable portions of the hides are going into solution. Several attempts have been made to solve this question, but up to the present none has been successful. A method which was tried last spring in Leeds is based on the fact that collagen, leucines and keratins, when hydrolyzed, give a different amount of di-amido-nitrogen in proportion to total nitrogen, and that this di-amido figure can be obtained fairly easily. The results, however, are not quite satisfactory in mixtures, and the method is too elaborate to be of immediate use for practical work.

Another question is to distinguish between hide substance dissolved by putrefaction and hide substance dissolved by the chemical action of alkalis. One might expect that putrefaction would lead to a higher degree of hydrolysis than chemical action, and that the acidity produced by the action of formaldehyde on neutral amido acids would allow of the determination of this degree of hydrolysis, and consequently the part which putrefaction plays in the dissolving effect. Careful experiments have.

however, shown that things are more complicated than might be expected, and that the above assumptions are not to be relied upon.

While work on those lines seems to be very necessary, new methods of unhairing are coming forward without the use of any alkali and without the necessity of such research as has been mentioned. In the new process of Röhm and Haas the hair loosening action is produced by enzymes. This method is similar in principle to the old method of sweating, where bacteria and enzymes, together with the ammonia formed by them, were the acting agencies. Further improvements may be expected in the methods of puering and bating and in their control. The valuable work done by Mr. J. T. Wood has helped a great deal in those particular processes. As to the swelling and pickling, and the action of acids on hide in general and their influence on vegetable tanning, the work in which Professor Procter is engaged, the acid swelling of gelatine, will no doubt be found to be of great importance. Another problem which is perhaps too theoretical to arouse the interest of the practical tanner is the theory of the tanning process itself. The correct view of this question will be of great practical advantage, and the wrong view will lead to very considerable difficulties. Two examples which show the danger of a wrong conception: About 100 years ago a chemist evolved a tanning theory which appears to-day rather silly, but as to the correctness of which the inventor was quite convinced. The hide, according to his views, consisted of two parts, a soluble one which could undergo putrefaction, and an insoluble one which resisted putrefaction. By repeatedly treating the raw hide with tepid water he intended to remove the soluble portion, and was so convinced of the correctness of his view that he started a plant and lost his money. Another example: A few years ago Dr. Fahrion, a German chemist, started a theory according to which the hide must be oxidized before the actual tanning process started, and this oxidizing effect was believed to accentuate the chemical affinity of the hide substance, so that leather was assumed to be a chemical compound of oxidized hide fiber and tanning agent. As a practical consequence of this view, patents were taken out to oxidize the pelt by means of hydrogen

peroxide previous to tanning. Experiments, however, have since shown that oxidization plays no part in the preliminary treatment of hide, and that the leather made from ordinary hide is identical with that made from oxidized hide, as far as relates to the degree of tannage, water solubles and properties of the leather.

To every practical man, the correct theory of tanning is of great importance. At the present time there are two entirely different views. The one is the purely chemical conception, and the other the colloidal conception of tanning. In the chemical conception only the actual chemical action is noted. Dr. Stiasny mentioned one or two arguments against this theory so far as vegetable tanning was concerned. Vegetable tannins precipitate gelatine, and that precipitate is presumed to be somewhat analogous to leather, but there is no precipitate formed when the two substances—gelatine and tannin—are chemically pure. Any chemical explanation of that fact would be difficult, whilst the colloidal explanation is very natural. The other theory of tanning assumes that it consists of two phases. The tannin is taken up by the hide, and then undergoes some secondary changes, by which it is rendered insoluble, which prevents it from being washed out again. In both vegetable and mineral tannages the changes are of a colloidal nature. Dr. Stiasny thought this theory much to be preferred to the chemical theory. Whichever theory be adpoted, one thing which prevents us from coming to a definite conclusion in regard to vegetable tannin, is the fact that we know so little about the constitution of vegetable tannin. Once the constitution of the vegetable tannins is settled we shall be able to solve many problems. Chemists cannot give any explanation as to why oak bark gives a different result from chestnut and so on. We are quite at a loss to explain all the characteristic differences in the leather produced by various tanning materials, but it is, of course, probable that these may be explained as soon as we find out more about the constitution of the tanning materials. At the same time we may find that the constitution has not much to do with the quality of the leather, but only in an indirect manner so far as the constitution affects the physical qualities, and the possible changes due to the secondary fermenting action.

We have to wait until the experts elucidate the matter, but there is another way by which it might be elucidated. We may be able to find other tanning materials, and if we knew the constitution of them we might modify that constitution. If these modifications introduced a difference in the effects we might be able to arrive at some decision for the standardization of tanning materials. If chemical products would give a commercial leather which was able to compete with the present tannins, it would not only solve theoretical questions, but practical ones at the same time. Such a solution had been found lately in a substance called Neradol. Formaldehyde with some vegetable tannins gives a precipitate, and not with others. Many non-tannins, after treatment with formaldehyde give all the tests of tannins, and the question to be solved was to find out whether he could obtain soluble products which could compete in price with the vegetable tannins. That last phase of the question required considerable time to elucidate and work out. It consisted of sulphonating phenols and condensing those substances with formaldehyde under such conditions that only soluble products were formed. The product was soluble in cold water, and no portion of it was insoluble. On testing it with iron salts, he found it gave a distinct blue color. Personally, he thought it was only one step in the direction of solving a big problem, and that in future there would be a greater variety of different tanning substances than we have at present. We shall, also, no doubt, be able to produce substances which will give modified tanning results for different purposes.

THE ACID DELIMING PROCESS.*

By Prof. H. R. Procter.

Acid deliming processes are now in almost universal use, not only for heavy leathers, but very often also for lighter leathers, as a preliminary to diminish the amount of puering and drenching required, or to economize the use of modern bating preparations; and in view of recent investigations on the action of acids and

* Tanner's Year Book, 1913. 75-9.

salts on gelatine and hide-substance, the chemistry of such processes seems to deserve more thorough study than it has yet received.

In outline it is very simple. It would seem only necessary to use sufficient of any acid to form a soluble salt with the lime to secure its adequate removal, and with careful chemical control this is to a large extent true, and in skilful hands even such dangerous acids as hydrochloric and sulphuric have been used perfectly successfully. If abundant clean water is used, and a quantity of acid slightly less than is necessary to combine with the total lime is gradually added to hides in rockers, or with some other form of gentle agitation, and sufficient time is given for its effect to be equalized throughout the hide, perfect deliming will result, no matter what the acid; even calcium sulphate being soluble in the large volume of water used, and the remaining trace of lime being easily dealt with by the acids of the liquors, or the subsequent bating process. If carbonation (air or water-blast) be suspected, or if the water be hard, it is best to add the whole acid before putting in the hides, as calcium carbonate is not rapidly attacked by very weak acids, and the slight swelling of the surface caused by the stronger solution will disappear if time is given. The temperature of the water has little effect on the removal of lime, but considerably influences the plumpness; for sole leather it cannot be too cold, while for light leathers, temperatures up to 80° or 90° F. are often advantageous. In deliming for subsequent bating with some modern bates such as oropon, it must be remembered that these are calculated to act best on hides in an alkaline condition, and the deliming must therefore not be too thorough. The required acid must be determined either by actual determination of lime in the hides, or by adding the acid in the first instance very slowly, till the cut just shows pink in the center when moistened with phenolphthalein solution.

It is when acids are used in excess, whether to save time, or to dispense with accurate chemical control, that the process becomes really complicated, because in these cases the hide-substance itself, as a base capable of combining with acids, takes part in the reaction. Hide-substance is what is called "amphoteric," that is, capable of acting both as a weak base with acids,

and as a weak acid with alkalis; but in the case under discussion only its basic character comes into play. If more acid be present than is actually needed to combine with the strong base, lime, the excess, or a part of it, combines with the hide itself, usually causing acid-swelling, and, later on, competing with the tannins in their attraction for the hide-fiber. With the strong acids, the effect is very marked; and extremely small excess causes the hide to swell dangerously, since acid-swollen hide tends to tan dark-colored, and of brittle grain; and it is this reason which has almost driven strong acids out of use except in the most scientifically managed yards.

If hide is placed in very dilute acid, it does not, as a strong base would, combine with the whole of the acid required to saturate it, for the water itself (or more strictly its hydrogen-ion) acts also as a very weak base, and competes with the hide for the acid, so that a balance or "equilibrium" results, the proportion of hide-salt to hydrogen-salt ("free acid") being less as the acid is "weaker" or the quantity of water is larger. Hence, if the acid is sufficiently "weak," and its dilution sufficiently great, the proportion taken by the hide is insufficient to cause dangerous swelling, and slight excess is much less harmful, and most tanners prefer to pay the much higher cost of organic acids rather than risk the heavy penalties of insufficient scientific control. There is also an easy means of still further weakening a naturally weak acid (practically inoperative with strong ones), by the addition of a suitable quantity of its neutral salt. It is not here necessary to enter into an explanation of this action, which has been previously discussed in these pages, and is well known to every modern chemist, so that we need only consider its results.

To take a definite case, if we add to a weak solution of acetic acid, an equal quantity of acetate of soda, it has the effect of reducing the acidity and swelling power of the solution to perhaps 1/80th of that of the acid alone; but we do not thereby neutralize any portion of the acid, which is still capable of removing precisely the same amount of lime as before the addition of the acetate. It is obvious that this reduction is very advantageous for safe deliming, and there is fortunately an inexpensive way of bringing it about. The action of acetic acid on

lime is to produce neutral acetate of lime, which acts similarly to the acetate of soda, so that all which is needed is to retain a sufficient quantity of the old liquor to restrain the action of the newly added water and acid, and to limit swelling to any required degree while completely removing lime. This method is equally applicable to formic, lactic, acetic, and butyric acids, though the largest proportion of old liquor will be required with the formic, and the least with the butyric to produce an equal limit of swelling. Which acid should be used is mostly a question of prejudice, and price per unit of acid-strength. The method is not suitable for boracic acid, which should always have fresh clean water, since it is naturally sufficiently weak, and its lime-salts are so little soluble that an old liquor becomes saturated and incapable of removing the lime-borates from the hide, which are carried forward into the liquors, where they produce much the same effects as the carbonates.

The indirect use of the strong mineral acids to liberate the weaker acids from their lime-salts, and enable them to be used a second time, has often been suggested, and has much to recommend it, as the stronger acids are very much the cheaper. We must not, however, overlook in this case the effect of the neutral salts of the strong acids which remain in the liquor. It has been shown by the writer that if hide treated with formic acid alone be placed in a strong solution of common salt the formic acid is practically entirely replaced by hydrochloric, of which as much as 3½ per cent. of dry HCl may be fixed. Whatever neutral salt of a strong acid is present in the deliming liquor will replace a certain proportion of the weaker acid in a similar way, and we do not know how far it is indifferent in tanning whether the hide-salt is a chloride, a sulphate, an acetate, or unaltered hide, though the swelling may be in all cases alike; and on this point properly conducted scientific research is urgently needed.

Several ways may be suggested to avoid the accumulation of soluble salts of strong acids in the deliming liquor, and the consequent fixation of the acids in the hide. The most obvious is to employ a strong acid of which the lime-salt is only slightly soluble, and both for this reason and on account of its cheapness, sulphuric acid seems the most suitable. The insolubility of the

sulphate of lime is still further increased, and at the same time the possibility of the fixation of what remains is diminished by retaining in the liquor a sufficiency of the lime-salt of the organic acid. The following method therefore seems practicable, though it necessitates some chemical control, and the most advantageous quantities can only be found by experiment.

For the first operation the organic acid only is used, and in order to avoid too much swelling, large excess of what is required to remove the lime must be avoided. For the second pack the amount of acid consumed by the first is ascertained by titrating a measured quantity of the liquor with caustic soda solution or saturated lime-water and phenolphthalein, and the liquor is made up again using the organic acid only, and perhaps to a somewhat greater strength than at first, as the danger of swelling is prevented by the accumulated lime-salt of the first operation. For subsequent strengthening a mixture of, say, three molecular parts of sulphuric acid with one of organic is used, and this can be continued till the liquor becomes too foul, the final strengthening before running away being made with sulphuric acid only, to economize the organic acid. Though organic acids have little solvent effect on the actual hide-substance a certain amount of animal matter will accumulate, mainly consisting of the partially dissolved substances brought in from the limes; but this in itself will have no injurious action, and putrefaction does not readily take place in acid liquors, though as an additional precaution an antiseptic such as carbolic acid (say 1-2 pounds per 100 gallons) or corrosive sublimate (2-4 ounces per 100 gallons) may be added; or a portion of boracic acid may be used in the strengthening mixture. The process sounds rather elaborate but would be much cheaper than the use of organic acid alone, and would be quite easy to a chemist, while, if systematically carried out, little attention would be necessary once the correct quantities were ascertained. If the hides plumped too much, the proportion of sulphuric acid should be lessened; if too flat, it might be safely increased.

For certain sorts of leather the pickling process with salt and acid is an advantageous way of deliming, but it is not applicable to sole-leather, and its consideration must be deferred.

STUDENTS' PRESENTATION TO PROFESSOR PROCTER.*

The students of the Leather Industries Department of Leeds University arranged an informal dinner on Friday evening, June 6, in honor of Professor Henry R. Procter. About 50 were present, including the students of the department, and most of the distinguished leather chemists of England. There were speeches from Dr. J. G. Parker and Mr. C. F. Muckenhirn, a student from Detroit, Mich. Mr. Harold Brumwell, a lecturer in the department, then made the presentation speech, on behalf of his colleagues and the students of the department. The gifts were a barograph, a thermometer, an arm-chair and a cafetière. An oil portrait of Professor Procter is being made, and will probably be presented at the time of the opening of the Procter Research Laboratory.

In his speech of reply and acceptance, the professor credited the success of the Leather Industries Department to Professor Smithells, of Leeds University, who was the founder of the department, and to the zeal of the students who had worked in it. He predicted that the next twenty years would see as great progress in the chemistry of leather manufacture as have been witnessed in the last twenty.

A toast to the Leather Industries Department was proposed by Mr. W. H. Beckworth, one of the first students in the department, and seconded by Professor Smithells, who said that Professor Procter's kind allusion to his initiation of that department of Leeds University made him feel that he ought to have the appearance of a patriarch. The late Mr. Beckworth wanted to know whether it was possible for the chemical department to do more for the leather industry than they were doing. Professor Smithells said his reply was to the effect that he could teach pure chemistry, but leather trades' chemistry was quite beyond his powers. He was not prepared to follow the fashion in those days of buying text-books on applied chemistry to get a few hours' start of the students and then teach them chemistry. There was only one course to pursue, and that was to procure the services of a man who was not only a chemist and possessed

* Condensed from *Leather Trades Review*, June 11, 1913.

sound practical knowledge, but who had cultivated a knowledge on broader lines of the chains connecting practice and theory. They had one man in view, and before long he was instructed to go to Newcastle to see Professor Procter. His instructions were that he should exercise any wiles and practice any art he could to secure Procter's services. Fortunately for the University he was successful. A small committee was formed to deal with the establishment of a leather industries' section, consisting of Mr. Flitch, Mr. Brown, Professor Procter and himself. With Mr. Flitch he made a continental tour to glean information in regard to applied chemistry, which in some parts of Europe had been further advanced than in England. They had a pleasant tour, and covered a considerable part of Europe. Afterwards they received the support of the Skinners' Company, and Professor Procter began his work. It was unnecessary to enlarge on the progress made since but it must be very gratifying to Professor Procter to be surrounded by affectionate pupils to do honor to him, when for some reason, best known to the University authorities, he must withdraw his services from the University at full juvenility. Professor Smithells caused some amusement by stating that Professor Procter and himself could not agree in everything, for while his friend was a firm believer that economics was an exact science, he was of the contrary opinion. But Professor Procter was a man of remarkable versatility, for he could converse on any subject under the sun. One gentleman, after a casual conversation with Professor Procter, asked him if he (Procter) was the professor of metaphysics. But to the whole University, to the Senate and to all concerned, the success gained by the leather industries department was a source of the highest congratulation. Professor Procter's success illustrated the great truth, that success in university teaching did not depend solely on appliances and apparatus, but on individuals. It was at one time a source of anxiety to them to know what to do when the Professor should retire, but by a stroke of enterprise they took time by the forelock, and managed to secure the services of the one man in the world who was fitted to succeed Professor Procter. He came, he saw, and he conquered. Like Professor Procter, he possessed

conspicuous modesty, and showed an enthusiasm for his work that gained for him the respect and attention of the students. He was not merely a chemist and a practical man, but a man of large ideas and in every way fitted to meet the responsibilities of a professor in a university. Continuing, Professor Smithells said he would like to remark that much importance was now attached to applied science, or the linking up of the abstract with the concrete. The professors who were in touch with the great industrial activities of the world were doing good work. and Professor Procter had done brilliant service in the science of the leather industry. They all regretted his departure, and wished his successor, Dr. Stiasny, and Mrs. Stiasny, long and successful life in the city of their adoption.

DR. STIASNY expressed his hearty thanks for the kind remarks about the Leather Industries' Department, also for the unnecessary references to himself, but he would prefer to confine his response to the Department. He believed that Leeds University was the first in the world to establish a leather trade department, and its position to-day was entirely due to Professor Procter. It was about 25 years ago that the new theories of physical chemistry of Van t'Hoff and others were published. They were rapidly assimilated on the Continent, but for some reason did not find favor in England for many years. It was a great thing for the leather industry that one man in England, who was then engaged in practical work, not only grasped these new theories almost at once but soon understood them thoroughly and translated Kohlrausch's work into English. That man was Professor Procter, one of whose serious studies at that time was devoted to astronomy. In fact, he progressed so far that he was invited to join a commission to India to undertake special investigations into this subject. Fortunately for the leather trade the professor did not go, otherwise the science of leather manufacture might be nearly in the same position as it was 30 years ago. Professor Procter's scientific research into the swelling of gelatine with acid has brought him fame as a physiological chemist. The wide knowledge of the Professor was remarkable, and Dr. Stiasny said he was astonished to find that an article from his pen appeared not long ago in the *Jugend Münchener*, a German

journal that might best be described as a mixture of the English journals, *Punch* and the *Studio*. It appeared that the editor of the *Jugend Münchener* had lately taken an interest in physical chemistry, and particularly in the theory of ionic equilibrium, on which the professor's article was based. Dr. Stiasny said he just mentioned that to show the professor's versatility. In these days, when work and scientific studies were more specialized than ever before, it was quite exceptional to meet a man of many attainments like Professor Procter. His great influence in the I. A. L. T. C. was undoubtedly due to his all-round qualities. The German chemists referred to him as their *altmeister* (old or senior master), but it would be wrong to connect age with that term, for the professor was still vigorous, tenacious and possessed of wonderful powers of imagination. It was no wonder, therefore, that the Leather Industries' Department at Leeds had flourished, and Dr. Stiasny thanked those who had toasted the success of the department, and also Professor Procter, on behalf of those in the department for all that he had done for them.

ABSTRACTS.

A Precision Viscosimeter. E. W. Washburn and G. Y. Williams, *J. Am. Chem. Soc.*, June, 1913, 737-50. The instrument described is a modification of the Ostwald viscosimeter (see this J., Jan., 1913, p. 49). The bulb into which the liquid flows is made of relatively large diameter, and the capillary is relatively long and of small diameter (0.5 mm.). The material is quartz, which is unaffected by some liquids which act on glass. The Silica Syndicate, Limited, 82 Hatton Gardens, London, will furnish duplicates.

The Mimosa Bark Industry of South Africa. J. G. Parker, *Tanners' Year Book*, 1913, 115-20. Information in regard to "wattle bark" in this article is practically identical with that abstracted in the June number of the Journal. Dr. Parker states that the Planters' Association of South Africa have not taken up the question of grading the bark. It is assumed that the best prices will be obtained for the lightest colored barks. The lighter barks are from younger trees, and the percentage of tannin is less in these than in the older bark. Dr. Parker analyzed three samples from trees aged four, five and six years. The percentages of tannin were 27.5, 31 and 36.5 respectively. The ground samples were submitted to a well-known salesman accustomed to arbitrate disputes in regard to this

material. He rated the third sample, highest in tannin, at the lowest price. The midde one was rated 60 cents a ton higher, and the first, which was lowest in tannin, at $2.40 per ton higher than No. 3. The color may be damaged by rain, etc., but in general the higher the percentage of tannin, the darker the color. The Tanners' Federations have asked the South African Government to institute a system of grading at the port of shipment.

Tanning in Vacuum. U. S. Patent, No. 1,065,168, issued to C. W. NANCE, of London, England, relates to a method of tanning in which the hides are placed in a liquor contained in an air-tight tank from which the air is then exhausted down to a pressure of not more than one inch of mercury, or one-half pound per square inch. It has been found that the tannage of hides is hastened by conducting it under reduced pressure. A hide which requires about five months to tan at atmospheric pressure, 15 pounds per square inch, will tan in two months at 13 pounds, in 40 days at 10 pounds, and in 25 days at four pounds, and in 20 days at one pound. If the vacuum be increased so that the pressure is only one-fourth of a pound per square inch, the time required is only two days. The great drop in time between one pound and one-fourth pound is explained by the fact that at this very low pressure the boiling-point of pure water is distinctly lower than that of the tanning solution. Under a pressure of one-half pound per square inch, water boils at about 77° F., so that it is easy to choose a state of temperature and pressure such that the water in the pores of the hide will boil, and so be expelled, and the tan-liquor will then penetrate the hide as soon as the pressure is a little increased. When this takes place, the hide-fiber combines with the tannin of the liquor, releasing the water, which is then evaporated as before. Glass cylinders are arranged in communication with the tanks, in which pieces of hide are placed. These may be removed whenever desired, and the condition of the hide examined. When a batch of hides is put in, the vacuum is carried up to the desired point before the liquor is introduced. From time to time some of the liquor is pumped off and fresh added. Mr. Nance claims for the leather produced by his process quality superior to that made by the ordinary methods. To produce the high vacuum necessary, a special form of exhausting apparatus is used.

Theory of Salt Stains. W. EITNER. *Gerber,* 1913 (39), 99-101, 113-5, 127-9. It was formerly assumed that salt was a sufficient preservative for green hides and that stains resulted either from impurities in the salt or from faults in the application. In general, boiled salt is considered best, then sea-salt and last, rock salt; exact investigation seems to confirm this. The chief differences in salt, however, lie in the denaturing materials; those which especially cause spots are alum, oxide of iron and mineral oils. The consumer has power to control this matter.

As to the manner of salting, it is important that this be done early, as soon as the hide has lost its life heat, best hastening by artificial cooling. A large share of salt stains may be attributed to bacterial action having advanced before salting. Another source of injury is insufficient salting and the leather manufacturer must frequently pay for this economy. Prof. Becker of Frankfurt has shown that some micro-organisms may survive in presence of salt in high concentration. Among these are genuine putrefaction bacteria also various spot-producing fungi. An important element in salting is the maintenance of high concentrations, especially when applied late. The action of dry salt is to withdraw by osmosis the fluids of the hide, blood and lymph, which are especially susceptible to decomposition and infection. The amount withdrawn is about 20 per cent. and to effect this, 10 per cent. green weight of dry salt is used, half of which flows away, the other half remaining in the hide as a five per cent. solution. This is insufficient preservative and is afterwards strengthened to 25 per cent. by addition of 15 per cent. (green hide = 100) more salt. For simple transportation, a total of 12-15 per cent. is considered sufficient salting; this reduction makes the risk of damage to the hide greater. It is customary to apply the entire quantity of salt at once; the fore-salting and withdrawal of the easily decomposed hide matter are dispensed with for the sake of sparing salt and labor, and to avoid disputes, over the rebate resulting from loss of weight by draining. This last is practically indeterminate, but the green hide loses four per cent. by a fore-salting with 10 per cent. salt. Although a large quantity of salt produces a high concentration in the bundle and protects the hide from most germs, it is safer to conduct the salting in two operations and drain the liquor. The most disagreeable consequence of under-salting is seen in the thicker part of the hide undergoing fermentation producing a hard and glassy leather, especially in the grain.

The author believes that salt stains are often caused by local drying during storage, causing a separation of salt crystals which mechanically rupture the grain. The deep seated wounds absorb larger amounts of tannin, dye and fat. This danger is greatest in bundled hides and can be prevented by keeping them moist. The stains caused by organisms can be readily distinguished by the microscope; instead of resulting by displacement of the fiber, they come from its corrosion.

As it is important that the hide be as free as possible from germs before salting, artificial sterilization is of great aid. This has been very successful with formaldehyde in Argentina. Sulphur dioxide, being also gaseous, may be used, but liquid or solid antiseptics are most suited.

W. J. K.

Kohinoor Gambier. W. Eitner. *Gerber*, 1913 (39), 141-3. Catechu in the extracts of Japonica and gambier has long been used as a light tanstuff for the completion of a weak tannage with bark. It was also used in sole leather manufacture for filling and giving weight. In this

case the crystalline catechin (catechuic acid) is the weighting element; the material is now too dear for heavy leather. For upper leather tannage the separation of crystalline catechin renders the grain brittle, the reverse in action to the catechu tannin which gives a soft mild leather. Another form of the catechin separates from hot solutions on cooling as a brown slime which hinders tannage and darkens the leather. This form is contained in Japonica and the crystalline form is gambier.

Lately the Wilsdorf Extract Factory (manufacturers of Triumph quebracho) have separated the catechin and put in the market a purified catechu tannin "Kohinoor-Gambier." This is suited for after tannage of all sorts of enamel leather which requires a light but thorough tannage in order to withstand the heat. With Kohinoor the time may be shortened to two days each in six vats, a maximum number. The absence of the catechin contributes to the mildness of the leather. For heavy enamel leather the tanning may even be finished in the drum. For dyed leathers the process may be made quicker with more latitude in the use of the drum. The liquors may be graded with precision by specific gravity, the tan-stuff being pure. Kohinoor comes in dark, glistening lumps soluble in cold water, although hot water is used for quicker work. After skiving or splitting and levelling an after tannage is applied with Kohinoor itself, or sumac for light shades. For weight leather, purified quebracho is better. For the combination sulphur tannage earlier described by the author (abstract this JOURNAL, 1911 (6) 257), Kohinoor is adapted; 6-14 vats with croupons. For heavier stock a lay-away is used at the end, lighter hides in the drum. For the after tannage of double bath chrome leather to give it good grain for currying, Kohinoor is applied together with oleate liquor in the drum.

W. J. K.

Neradol. W. EITNER. *Gerber,* 1913 (39), 155-7, 169-71. The author translates Stiasny's article in the *Leather World* (reprint, ante, p. 208) concerning his own invention "Neradol" and then goes on to describe his own experiments.

Neradol is a dark, viscous mass smelling slightly of carbolic acid, sp. gr. 27° B. and dissolving easily and completely in water. After several days standing the light brown solution separates a gray-green sediment. Like vegetable tans, Neradol ppts. albumin and gives dark colorations with ferric salts. It analyzes:

Absorbed by hide-powder	22.10
Unabsorbed by hide-powder	40.32
Water	37.58
Ash	18.14

Neradol has an acid reaction containing 2.936 per cent. neutralizing and swelling acids of which 2.055 only neutralize. This acid reaction in part explains the behavior of Neradol in use. Its action towards the albumin of the hide is quite different from that of vegetable tans and

most mineral tanning agents. If white hide be treated with even very concentrated solutions, there is no contraction of the grain which remains smooth and soft. In course of time swelling ensues as a result of the acid character and it is important that this does not readily fall down; this may be utilized but on the other hand is a disadvantage with unsuitable after-treatment. The swelling power of the liquor does not appear to decrease on use but remains constant, the tanning component being consumed while the swelling component remains. The tanning action of Neradol depends little on the concentration of the liquor. The product differs from that of vegetable tannage and also in part from mineral tannage, being intermediate between tanned hide and flesh. With thick hide it is difficult to tan entirely through and obtain a uniform section. The outer part is light colored and opaque while the interior is transparent, the entire section resembling that from an incomplete alum tannage. Under the microscope the outer fibers are seen to be dense and surrounded by a light colored mass protecting them from exterior action. Although the interior is less dense, it withstands boiling with water, resembling formaldehyde leather. The acetic acid test renders the inner section more transparent but there is no swelling as usual in incomplete tannage. The alteration in the gelatine substance is like that produced by formaldehyde, although less, the latter being carried out in presence of alkali.

The author could not fully tan thick hides with Neradol alone but succeeded with lighter hides and especially with those of loose texture like sheep skins. These were notably increased in density and resistance. A hide treated with Neradol is stiff on drying but not horny, resembling alum leather and like it can be softened by working and remains thus even after wetting and again drying while alum leather becomes stiff again. Neradol further differs in not becoming elastic which although unsuited for glove leathers, renders it fit for other purposes.

In practical tannage, experiments were made with sole leathers, and working methods established. Limed hides were de-limed with HCl and washed to avoid the formation of gypsum from the sulphuric acid of the Neradol. The results showed Neradol suited for the fore-tannage of sole-leather. The liquors have a strength of 1-2° B. (25-50 K. in 1,000 liters water). In these the hides are suspended 24 or 12 hours with frequent handling which may be spared by using machinery. The grain is not altered in structure but becomes protected from too rapid action in the following vegetable tannage which so often produces a brittle grain. This is sufficient when the grain becomes opaque resembling porcelain. This coating of the grain fiber by the Neradol also strengthens it against weakness originating before tannage, from de-liming with acids, bating, unfavorable water, etc. For vache leather where a brittle grain is to be shunned, the fore-tannage must proceed slowly in weak liquors. If the grain be fixed with Neradol, the tannage can be pushed in stronger liquors and considerable latitude is possible in their preparation.

It is necessary, however, that they be clear, for sediment especially clogs a fiber coated with Neradol. The Neradol bath can be used repeatedly but must be generously re-strengthened since it is rapidly consumed. When the bath becomes too acid a new bath must be prepared but the acid bath can still be used for hard and solid sole-leathers. For these leathers, Neradol and tan-stuff together are let act on the hide. 25 k. Neradol are added to 1,000 l. liquor in the first weak vat and the hides run through the handlers without addition to the stronger vats. This is fairly equivalent to the use of a separate Neradol bath for the fore-tannage. A used Neradol bath can be utilized in the preparation of the liquor for the upper vat of a fore-tannage together with extract. If old, partially exhausted liquors are employed (sour liquors) the Neradol bath is kept permanent by addition each time of fresh Neradol in the upper vat.

Neradol imparts a white enamel to the grain serving as a foundation and brightening the color of dark tan-stuffs. It accelerates tannage but as this may be secured otherwise, its chief value is for improving quality, giving a fine, elastic grain to vache leather and very solid, but not brittle sole leather, and withal, high rendement. With thinner leathers, the fibers may be completely encrusted, permitting a uniform tannage in combinations. The Neradol is added to the liquors throughout, and being rapidly consumed, is often replenished, one-fourth to one-half per cent. in the weak liquors, one per cent. at the finish. In the combined tannage, the author found Triumph quebracho to give the best product, excellent to curry for upper leather and able to take much fat. Sumac extract gave good russet and saddlers' leather. This combination is light proof unlike others, Neradol being sensitive to light. Sulphite cellulose gave stiff, hard leathers.

No advantage was found in combining Neradol with chrome tannage; the leather is dense but rather stiff and not improved by liquoring. Alkalies in general are prejudicial to leather containing Neradol which must be taken account of in soaping upper leather: an acid oleate stuffing is better. Neradol is used for bleaching; its real action is to lighten dark tans through covering effect, and unlike other agents it adds weight. The leather is suspended in or brushed with a 5 per cent. solution. Neradol also serves as a dressing and on rolling sole-leather it acquires a high gloss.

In conclusion, Neradol is no tan-stuff, nor can it replace the vegetable tannins. It is an excellent auxiliary, however, and will probably reveal still more virtues.

W. J. K.

Chestnut Wood Extract. LEOPOLD POLLAK. *Collegium,* 1913, 291-9. The commercial extract is rarely treated chemically and may be considered a pure product, producing a uniform leather. The tannin content of the wood varies according to situation, age, etc., but has no significance

for the factory where a constant average of 7 to 9 per cent. obtains according to the country. The Corsican Chestnut (Holz II, rotes Holz) differs slightly, the wood being streaked with red. Some laboratories reported sulphite cellulose in an extract made from this wood (abstr. ante, p. 264), relying on the Procter-Hirst reaction. The author found the substance giving the reaction present in the red wood itself; a Corsican wood (White I), 11 per cent. tans gave no reaction while a red wood (II) of 13.9 per cent. tans gave a turbidity. In the factory, this substance is found in the first concentrated liquors, but the last thin liquors (0.6 per cent. tans) do not give the test. Since these liquors are produced at the highest pressure, it may be concluded that the reacting substance does not come from pressure extraction. Further experiments showed that after blood decolorizing, the extract no longer gave the reaction.

II. *Sugar Content.*—The methods used by Jedlicka (abstr. this JOURNAL, 1909 (4), 162) with oak-wood were here employed. Besides the two forms of sugar determined after freeing the extract from tannin, a third sugar "number" was determined by inverting the total extract; this is considered useful in factory practice. Ten extracts (separate analyses given) taken from the same manufacture during three months averaged:

Tans	27.6	Grape sugar (I)	4.3
Non-tans	11.6	Cane sugar (II)	4.3
Insoluble	0.8	Sugar (III)	2.4

Sugar III from four hours inversion of total extract fluctuated greatly (0.5 to 4.4). Whether this sugar comes from substances pptd. together with the tans by the Pb acetate or by hydrolysis of a glucoside tan, or in both ways, the author like Jedlicka, considers unsettled. Experiment showed the amount of Sugar III was much less after blood decolorization.

W. J. K.

Proposed Method for the Volumetric Determination of Sugar in Tanning Materials, Liquors, Leather, etc. W. APPELIUS and R. SCHMIDT. *Ledertechn, Rundschau,* 1913, 153-5. Von Schroeder proposed that the usual Fehling reduction according to Allihn be extended to one-half hour boiling to insure complete reduction of the sugars, and prepared corresponding tables (differing from Allihn's) for computing the sugar from the reduced copper. (*Dingl. polyt. Jour.,* 1894 (293) Heft, 10.) This table and working details have been published as a monograph by Paessler. To avoid the laborious gravimetric determination of the reduced copper, the authors determine volumetrically the copper in the Fehling solution before (blank test) and after reduction, the difference measuring the reduced copper. Excess KI is added and the liberated iodine (1 at. I = 1 mol. $CuSO$) titrated with thio. (Note: this excellent method has been in use for years, published by Schoorl, Riegler and perhaps others; *Abstractor*). To one gram extract at least three cc. basic lead acetate

(sp. gr. 1.235-1.24) are added and let stand with frequent shaking ¼ to ½ hour. To ppt. the Pb, satd. Na_2SO_4 sol. equal in volume to the acetate is used. For sulphited extracts, 3-4 cc. acetate are taken to each gram. Example: 15 grams chestnut extract dissolved in 250 cc. H_2O, 50 cc. acetate added, filtered after ½ hour; to 100 cc. filtrate 20 cc. Na_2SO_4 added, filtered; 10 cc. filtrate used for direct reduction. For inversion 50 cc. of Pb-free filtrate boiled ½ hour with 10 cc. H_2SO_4 (one pt. conc., five pts. H_2O), neutralized with conc. NaOH, made up to 100 cc., 20 cc. taken for reduction.

Blank.—15 cc. $CuSO_4$ (Fehling), 15 cc. alkali tartrate (Allihn), 45 cc. H_2O mixed and rinsed into a small Erlenmeyer containing 10 cc. KI (80 grams to 250 cc. H_2O) and 15 cc. dil. H_2SO_4 (1:2). This is slowly titrated with N/10 thio (standardized against $K_2Cr_2O_7$) till only pale yellow, starch then added and titration continued until colorless, the gray white of the CuI ppt. appearing.

Sugar Titration.—The sugar sol. should correspond to about ¼ per cent. glucose, equivalent to 10-12 cc. thio; the extract charge above conforms to this. Leather washings are generally diluted instead of concentrated as usual. As in the blank, 15 + 15 cc. Fehling are used, together with 35 cc. H_2O, 10 cc. sugar sol., and heated ½ hr. in a boiling water bath. The sol. is then quickly cooled and titrated as in the blank without filtration. The authors use arbitrary standard sols. and an indirect computation, consistent, however, with the simple relation, 1 cc. N/10 thio = 63.6 mg. cu.

Numerous duplicate analyses by gravimetric and volumetric methods are quoted; they check well.

W. J. K.

Action of Cellulose Extract Upon Quebracho Extracts. H. WINTER. *Ledertechn. Rundschau,* 1913, 161-3. Yocum and Faust, Sody and others have found that on mixing tannin extracts with cellulose extract, the total tannin content is lowered. On the other hand claims are published for a certain brand of cellulose extract rendering quebracho extract cold soluble. The author has subjected this question to experimental test. The extract in question is designated Cellulose I. To ascertain if this differed from ordinary cellulose extracts, a separate extract was specially made, designated Cellulose II. Solid Argentine quebracho with especially high insoubles was used = Quebracho A; after standing some time subject to change, a second sample was taken = Quebracho B. Analyses:

	Cellulose I	Cellulose II	Quebracho A	Quebracho B
Tans	25.1	19.1	68.5	70.3
Non-tans	22.0	13.3	4.4	4.6
Insoluble	0.0	0.0	10.0	10.0

For the first experiment 250 grams Quebracho A were mixed with 250 grams each Cellulose I and II with one liter water, then warmed to complete solution on the water bath.

	Mixture I		Mixture II		Quebracho I		Quebracho II	
	Mixt.	Singly	Mixt.	Singly	Mixt.	Diff.	Mixt.	Diff.
Tans	47.1	46.8	45.0	43.8	69.1	+0.6	70.9	+2.4
Non-tans	16.9	13.2	11.6	8.8	11.8	+7.4	9.9	+5.5
Insoluble	0.8	5.0	0.7	5.0	1.6	—8.4	1.4	—8.6

The analyses of the mixtures are shown in the left-hand columns computed for comparison on the original water content. Assuming that the cellulose extract remains unaltered, this is deducted from twice the analytical figures, leaving the analysis of the quebracho alone (after mixture) as shown in the right-hand column. It is seen that both cellulose extracts lower the insolubles of the quebracho from 10 to about 1.5 per cent. and that about a third of this loss goes to increase the tans.

Experiments were next made with mixtures of 500 grams. Quebracho B with 500 grams each of the cellulose extracts and one liter water heated two hours at two atmospheres over pressure.

	Mixture I		Mixture II		Quebracho I		Quebracho II	
	Mixed	Separate	Mixed	Separate	In mixt.	Diff.	In mixt.	Diff.
Tans	51.8	47.7	49.4	44.7	78.5	+8.2	79 9	+9.6
Non-tans	13.1	13.3	9.1	9.0	4.2	—0.4	4.9	+0.3
Insoluble	0.8	5.0	0.0	5.0	1.6	—8.4	0.0	—10.0

It is seen that with Cellulose I, the solvent action is the same and with II it reaches the maximum. Almost all the increased solubles appear as tannin, in one even some non-tans have become tannin. This is improbable and more likely an error. There was no SO_2 present. To correct the results for the effect of pressure upon the cellulose extracts, these were heated separately in the autoclave and the figures used in re-computing the effect upon quebracho in the preceding experiment.

	Cellulose I		Cellulose II		Quebracho I		Quebracho II	
	Pressure	Diff.	Pressure	Diff.				
Tans	25.3	+0.2	20.5	+1.4	78.3	+8.0	78.3	+8.0
Non-tans	21.8	—0.2	12.3	—1.0	4.4	—0.2	5.9	+1.3
Insoluble	0.0	—	0.0	—	1.6	—8.4	0.0	—10.0

The gain of tannin in each is 8 per cent.; this was confirmed by another autoclave solution. As it is inconvenient in practical work to heat under pressure, an experiment was made in heating another sample of last mixture at 102° in a salt water bath, this being a temperature easily obtained by direct steam. The result also showed a high gain in tannin.

	Total mixt. I	Total mixt. II	Quebracho I		Quebracho II	
			In mixt.	Diff.	In mixt.	Diff.
Tans	52.0	49.0	78.9	+8.6	78.9	+8.6
Non-tans	13.6	8.8	5.2	+0.6	4.3	—0.3
Insoluble	0.8	1.0	1.6	—8.4	2.0	—8.0

In these researches the appearance of the extract obtained was in part at variance with the analysis; the treated extract showed in one case a sediment amounting to one-half the volume and so dense it could not be

poured out directly. Paessler and Veit have made an exhaustive study of such conditions (abstract this JOURNAL, 1908 (3), 358). The author has followed the methods specified but filtering through candles instead of paper; additional weak liquors were examined, the minimum solubility for most treated extracts being below 1° B.

The second line of the following table gives solubles reckoned according to the original analysis.

Gravity B°.	For analysis	0.1	0.3	0.5	0.75	1.0	2.5	5.0	7.5
Solubles, grams per liter	4.0	8.0	12.0	16.0	20.0	24.0	50.0	100.0	142.0
Insolubles, per cent.									
Cell. I, quebr. B, 102°	0.8	1.4	6.4	2.8	6.7	6.4	3.6	3.5	—
Cell. II, quebr. B, 102°	0.7	6.0	6.8	2.4	7.2	4.5	3.4	1.3	1.2
Cell. I, quebr. B, pressure	0.1	0.4	0.3	1.4	4.1	7.5	unfilterable		
Cell. II, quebr. B, pressure	0.0	0.8	1.1	1.5	1.1	0.2	2.6	3.0	3.3
Quebracho B alone	10.0	18.7	22.7	unfilterable					
Argent. extr. (Paessler.)	9.0	—	—	—	—	17.1	24 9	32 3	32.3

In conclusion, contrary to previous publications, at least with solid Argentine quebracho there is an increase of tannin on addition of cellulose extract which is greatest on mixing at boiling temperature. Quebracho extract is not rendered totally cold soluble; in one case this was attained by pressure treatment.

W. J. K.

PATENTS.

Composite Leather. U. S. Patent, No. 1,065,028. A. L. CLAPP, Braintree, Mass., assignor to Hide-Ite Leather Co., Brockton, Mass. Leather scrap is treated with alkali to loosen the fibers and dissolve the gelatine and then treated with an oil capable of being saponified by the free alkali present. The mass is then treated with a substance which renders the soap insoluble.

Leather Compound. U. S. Patent, No. 1,065,691. F. W. KREMER, Carlstadt, N. J. The materials used are new and reclaimed rubber, reinforcing fibers of vulcanizable material, antimony, lime, magnesia, zinc oxide, and asbestos.

Leather Rolling Machine. U. S. Patent, No. 1,067,164. Leather Working Machine. U. S. Patent, No. 1,067,165. Both to GEO. A. DOBYNE, assignor to the Champion Shoe Machinery Co. of St. Louis.

Manufacture of Leather and Leather-like Products. W. SPALTEHOLZ and K. HARING, Hersfeld, Germany. Hide is dehydrated with alcohol and impregnated with rubber.

Process for Treating Hides and Skins. British Patent, No. 5,350. F. RAMPICHINI, Trieste, Austria. A cementing process for leather.

Method of Ornamenting Leather. British Patents, Nos. 5,117 and 5,214. R. RIBOT, Paris. After being dyed, leather is coated with a tough, hard adhesive material of the same color, the base of which is linseed oil and litharge.

Sectional Roll for Leather Work. U. S. Patent, No. 1,066,913. A. H. KEHRHAHN, Frankfurt, Germany.

Pneumatic Roll for Leather-working Machines. U. S. Patent, No. 1,067,-607. HENRY A. HOLDER, Lynn, Mass.

Knife-adjusting Mechanism for Bark-removing Machines. U. S. Patent, No. 1,068,371. T. W. SIMPSON, Grand Rapids, Wis., assignor to G. E. Foster and Van A. Wallin.

Tanning Sole Leather. U. S. Patent, No. 1,067,796. PIERRE CASTIAN, Renaix, Belgium. The process consists in tanning first with chrome then with vegetable tan, and then waxing the leather.

Clarification of Quebracho Extracts. British Patents, No. 7,389 and 7,698. A. REDLICH, Vienna. Insolubles are removed by centrifugal treatment.

Hide-working Machine. U. S. Patent, No. 1,068,031. ROBERT E. WHITNEY, Winchester, Mass.

Treatment of Hide, etc. British Patents, No. 6,790 and 6,791. A. H. HENDERSON, Baltimore, Md. The same as U. S. Patents 1,020,497; 1,020,-498 and 1,020,499; see JOURNAL, 1912, p. 284.

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THE ELECTROMETRIC METHOD FOR THE MEASUREMENT OF ACIDITY.[1]

By Lloyd Balderston.

The classification of substances as electrolytes and non-electrolytes has been in use for many years, but the explanation of the difference between these two classes is comparatively recent. We say now that an electrolyte conducts electricity because some of its molecules have been split into parts, each part carrying an electric charge, and that the electricity passes through the electrolyte in the form of these charges carried by the *ions*, as the charged particles are called. Acids, bases and salts are ionized to a greater or less extent when dissolved in water,[2] and many substances are capable of being ionized by heat in the absence of water. The degree of ionization of a dissolved substance depends on the nature of the substance, and is in general greater at higher temperatures. It also depends on dilution, and solutions of many substances may be so far diluted that the molecules are all ionized. With hydrochloric acid this point is reached in the neighborhood of 0.01 normal.

This theory of solutions, the theory of electrolytic dissociation, has given a new meaning to the fact that chemical reactions take place for the most part only when one or both of the reacting substances has been liquefied. It would now seem that only ions, that is, split off portions of molecules electrically charged, can react. Substances which yield hydrogen ions are called acids, and the "strength" of an acid depends on its degree of ionization at a given temperature and dilution, the stronger acid being more fully ionized than the weaker under the same conditions.

When we speak of the acidity of a liquid, one meaning of the term relates to the number of hydrogen ions per unit volume in the liquid, or the hydrion concentration of the liquid, as it is called. Thus an acid solution whose normality is 0.01, if the acid is completely ionized at that dilution, has a hydrion concentration of 0.01, or 10^{-2}. In this last expression, the 2 is called

[1] Read at the Ninth Annual Meeting of the *A. L. C. A.*, Washington, D. C., December 6, 1912.

[2] Other solvents cause ionization, but none to so great an extent as water.

the "hydrion index." Solutions whose normality in hydrogen ions lies between 0.01 and 0.001 have a hydrion index between 2 and 3.

In another sense the acidity of a liquid means the whole amount of acid present in the liquid and capable of being neutralized, or, as we say, total free acid. This latter quantity may be much greater than the former, since if we begin to add alkali to a solution containing acid which is only partly ionized, the ions enter into combination with the base, and more molecules are ionized. If we continue to add alkali, the acid is finally used up, although only a small part of it may have been active at any one time. This is what happens when we determine the acidity of a liquid by titration, and the end-point for different indicators is different. Thus a liquid which is neutral to methyl-orange will be acid to phenolphthalein.

The scheme of the electrometric method is to estimate the actual hydrion concentration of the liquid by measuring the difference of potential between the liquid and a "hydrogen electrode." The method was first worked out by Bottger in Ostwald's laboratory in 1897; improved by Bjerrum in 1905,[1] and further improved by Sφrensen and others since. In practice,[2] the cell employed has for its positive electrode Ostwald's normal calomel electrode, consisting of mercury covered with a layer of mercurous chloride, lying in a normal solution of potassium chloride. This electrode is joined to the liquid whose hydrion concentration is to be measured by a capillary tube filled with 3.5 normal potassium chloride, a solution which diffuses very slowly. The hydrogen electrode consists of a platinum plate coated with platinum black, so arranged that a current of hydrogen is made to flow past it, so as to saturate the platinum black with hydrogen. In the diagram (Fig. 1), M is mercury, into which the platinum wire projects, C is the layer of calomel, and K normal KCl solution, extending as far as the 3-way cock S. The capillary T is filled with 3.5 normal KCl. Pure hydrogen from any convenient source flows in at E past the platinum plate P (which is connected to the binding post marked —) and bubbles out through the liquid in the beaker. When the plat-

[1] Zeit f. Phys. Chem. 53, 428.

[2] Sφrensen, Enzymatic Studies, abstr. *J. A. L. C. A.*, Mar., 1911, vol. VI, p. 138, and Wood, Sand and Law, p. 117.

inum electrode is saturated with hydrogen, the difference of potential between it and the liquid at a given temperature depends on the hydrion concentration of the liquid. As the number of hydro-

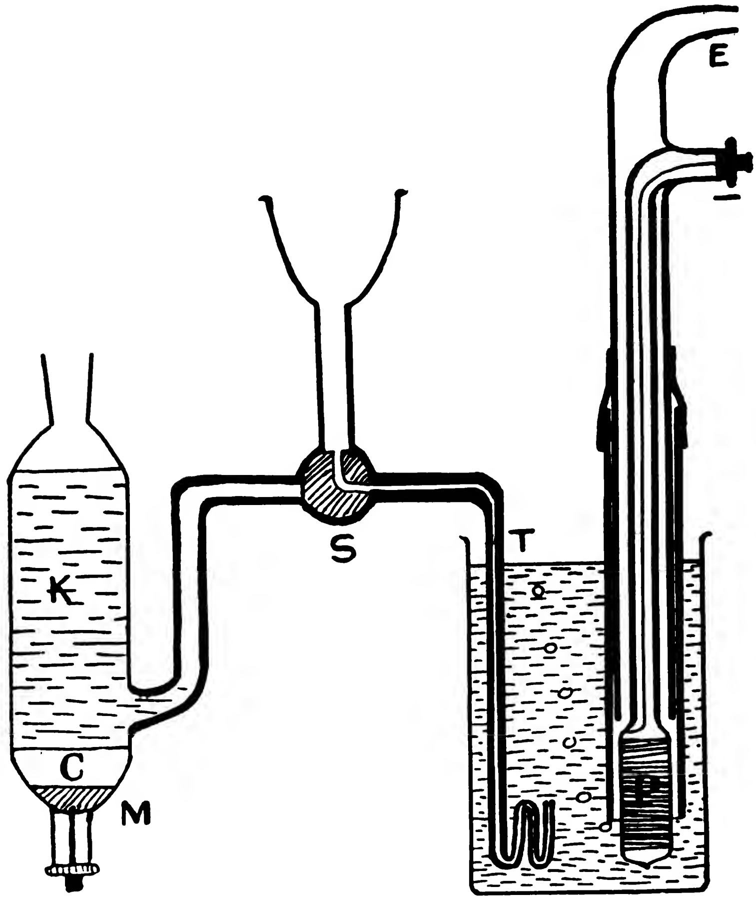


Fig. 1.

gen ions in the liquid increases, it approaches the same potential as the hydrogen electrode. Greater acidity therefore corresponds to lower e. m. f. of the cell.

The connection between the e. m. f. of such a cell and the hydrion concentration of the liquid at 18° C. is given by the equation[1] $\pi = 0.3377 + 0.0577\ p_{\mathrm{H}}^{+}$, in which π is the e. m. f. of

[1] Sørensen, *Journal A. L. C. A.*, VI, 264.

the cell, and p_H^+ is the "hydrion index" of the liquid. This last term, as has been stated, is the number denoting the negative power of 10 which represents the normality of the solution in hydrogen ions.

The apparatus exhibited is that devised by Wood, Sand and Law and described in their papers, reprinted in the *Journal* of the *A. L. C. A.* for March and September, 1911.

Difference of potential may be measured in a variety of ways. In practice, the method most used is indirect. A high resistance galvanometer is placed between the points whose difference of potential is to be measured, and we estimate the difference of potential by the current which flows through the galvanometer. The instrument is called a voltmeter, and is graduated in volts, although the thing it really measures is current flow. We could measure the pressure of water in a main by boring a very small hole in the pipe and measuring the quantity of water that flowed out in a minute. Having determined how much water per minute flowed through a hole of a certain size, under various pressures, from one pipe, we could bore a hole of the same size in another pipe and judge of the pressure of water in it by the water flow. A vessel graduated so that the first division marked the quantity of water which would flow from a hole of the standard size in one minute under a pressure of one pound per square inch, the second division the quantity for a pressure of two pounds per square inch, etc., would enable us to read pressures directly without calculation, just as the voltmeter enables us to read volts directly. Most commercial voltmeters work on this principle. The resistance of the instrument is made so high that all other resistances involved are negligible in comparison.

If other resistances in the circuit are very high, the voltmeter will not do. Our water pressure scheme would do very well for a six-inch main, a two-inch or even a one-inch pipe, but if applied to a pipe whose diameter was only one-sixteenth of an inch, it would probably fail because friction inside the pipe would hinder the flow, and the smallness of the test hole would no longer be the only hindrance.

In the cell above described, the internal resistance is consider-

able and also varies very much, so that the voltmeter method would not be satisfactory for measuring its e. m. f. We therefore resort to the potentiometer method. There are several forms of potentiometer, but all of them involve balancing the e. m. f. to be measured against a known or measurable e. m. f. Perhaps the simplest and most accurate form is illustrated by the diagram (Fig. 2). Water at a known constant pressure can be admitted to the cylinder A and acts on the piston P. The pressure to be measured is admitted to the cylinder B and acts on the piston Q. The knife edge E under the beam C D is adjusted so that the forces exerted by the two pressures balance. Now if the cylin-

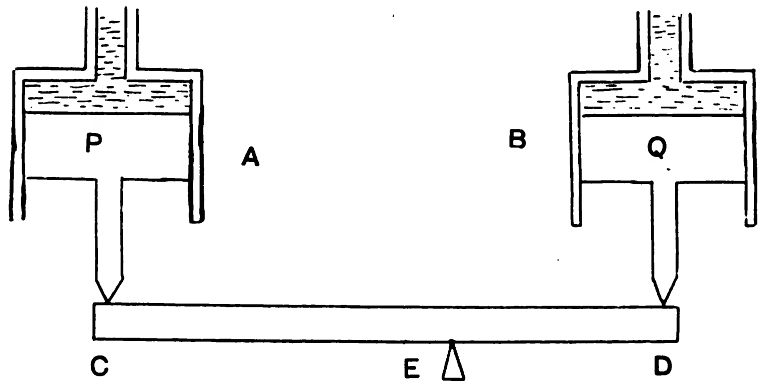


Fig. 2.

ders are of equal size, the pressures are inversely proportional to the lengths CE and ED. In the potentiometer, the variables to be adjusted are electrical resistances instead of lengths, but the water analogy explains the method fairly well.

The potentiometer of this apparatus is somewhat modified so as not to require the expensive standard cell which is an essential in the typical and most accurate form. Let us suppose in Fig. 3 that the cylinders and pistons are arranged as before, but the edge E is fixed at the middle of the beam. Pressure on P is due to water from a reservoir R whose height is adjustable to balance the pressure on Q. When this balance has been reached, the test hole V is opened, and the water flowing into the graduate G in one minute indicates directly the pressure on P and Q.

In this apparatus, the e. m. f. against which we balance the cell

is not fixed and known, but can be varied at will, and is always measured by a voltmeter. The diagram (Fig. 4) shows the actual arrangement. C is a dry cell, AB a resistance wire, P a movable contact, M the cell before described, with calomel and hydrogen electrodes, V a voltmeter always in circuit and measuring the difference of potential between A and the variable point P, and E a capillary electrometer which is short circuited except when the key K is depressed, when it is thrown into circuit with the other parts of the apparatus. When K is depressed the cell M tends to drive current around the circuit MSEKAPM, while the difference of potential between A and P tends to send

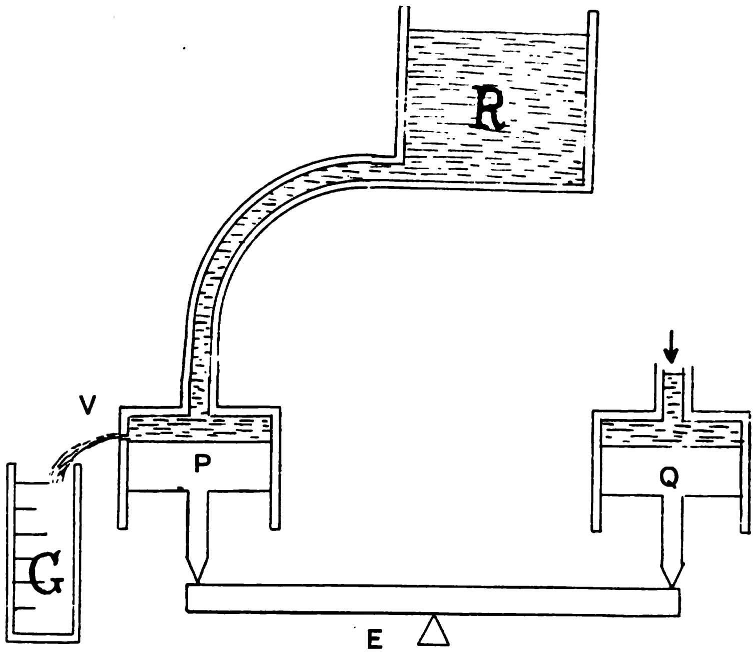


Fig. 3.

current around the same circuit in the opposite direction. By sliding the contact P and watching the electrometer, balance is established, and the e. m. f. of the cell M is read directly on the voltmeter.

The capillary electrometer is shown in diagram in Fig. 5. A platinum wire is sealed into B, which is full of mercury. A is

filled with dilute acid and has a platinum wire sealed in. The two are connected by a capillary tube, and this tube is partly

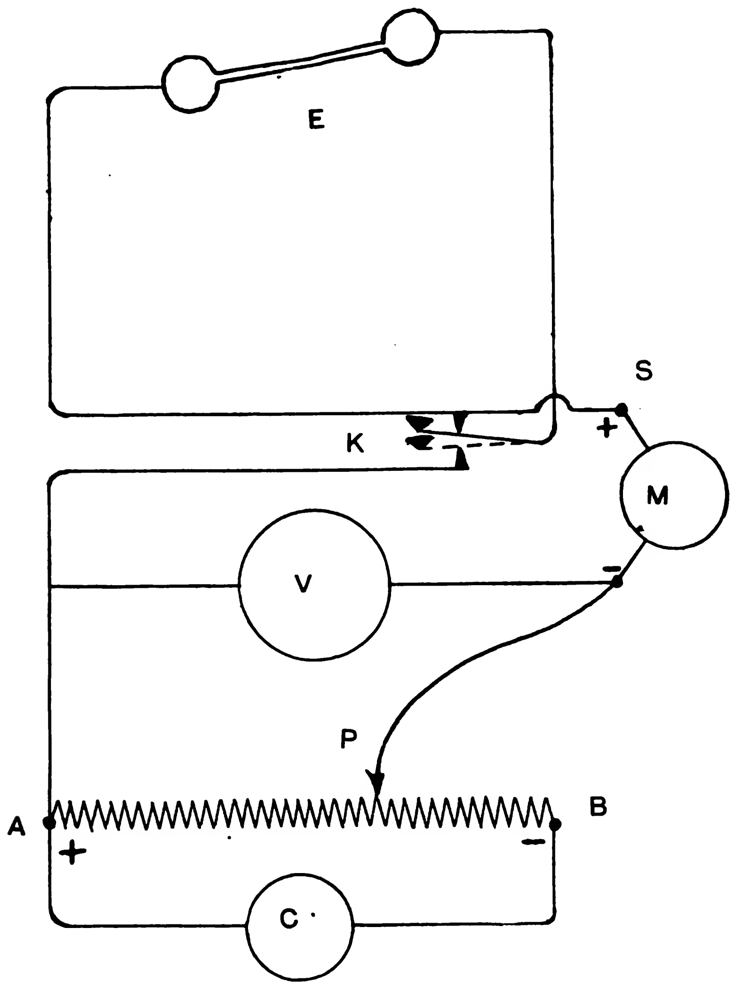


Fig. 4.

filled with mercury and partly with dilute acid by tipping the instrument. If the wires are connected to a source of e. m. f. the end of the mercury column tends to move from + toward —. The instrument may thus be used in the same way as a zero galvanometer.

In using the apparatus, hydrogen must flow through the hydrogen electrode for about half an hour in order to saturate the platinum black. To take a reading, depress the key K and quickly slide the contact P in such a manner as to bring the mercury in the electrometer back to its rest point. Depress the key again and again, a second or two at a time, adjusting P so that no motion of the mercury is observed when K is depressed. After a few minutes depress the key again. If no motion is observed, a reading of the voltmeter may be taken. When a second measurement is to be made, if the new solution is quickly substituted for the old, a reading may be taken after one or two minutes.

If a titration is to be made, first find the end-point for the indicator with respect to which neutrality is to be determined, as follows: Half fill a beaker of suitable size with a clear acid solution; put the beaker in place on the apparatus with the hydrogen flowing; add some of the indicator chosen; run in alkali until the end-point of the indicator is reached. Now adjust the apparatus to balance, and read the voltmeter. A little time is required after the last alkali is added before the e. m. f. settles to its final value. The reading thus obtained is the end-point at the given temperature for the indicator chosen. For phenolphthalein at 17° C. the end-point is about 0.69 volt. For methyl-orange at the same temperature, the end-point is not much above 0.50 volt. To illustrate the influence of acidity on initial reading, a series of readings was taken with HCl and H_2SO_4 of various dilutions. The readings for both were the same, but none are what they would have been at the standard temperature. They were too

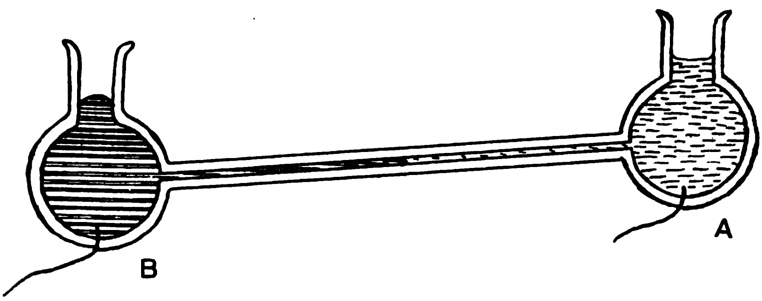


Fig. 5.

cold. The influence of temperature is considerable, but it can be avoided by determining the end-point for the temperature at which the work is to be done, and then having the solutions tested all at the same temperature. The series of readings mentioned was as follows: (the last three being taken at somewhat lower temperature than the others): N/1, 0.300 volt, N/2, 0.314, N/5, 0.332, N/10, 0.345, N/20, 0.360, N/50, 0.379, N/100, 0.395, N/200, 0.400, N/500, 0.425, N/1000, 0.435. Two per cent. of NaCl added to N/20 acid produced no change in reading. The same amount added to N/500 acid increased the reading from 0.425 to 0.427.

The result with N/20 acid and 2 per cent. salt seems surprising. It is well known that N/20 acid causes hide to swell strongly, and that the addition of 2 per cent. of salt almost entirely prevents the swelling. These facts are explained by saying that the salt hinders the ionization of the acid. One would therefore naturally expect that N/20 acid without salt would show a higher hydrion concentration than after the addition of neutral salt, but this seems not to be the case.

Very close duplicates may be obtained in titrating either acid or alkaline solutions with the apparatus, and for dark colored solutions, the method has decided advantages over spotting out on test paper. With regard to its possible use in titrating tan liquors, something has already been said in the report of the acid committee in the JOURNAL for December, 1912. It is easy to get good duplicates, and if we can find out just what the results mean, it is not impossible that we may be able to use this method to good advantage in the examination of tan-yard liquors.

(Since this paper was read, Dr. Joel H. Hildebrand has published a comprehensive paper on the same general subject, entitled, "Some Applications of the Hydrogen Electrode in Analysis, Research and Teaching", *Journal of the American Chemical Society*, July, 1913. His paper was read at the meeting of the Society at Milwaukee, March 28, 1913.)

THE ANALYSIS OF VARIOUS EAST INDIAN TANNED HIDES.*

By M. C. Lamb.

During the past few years the writer has often been asked by interested leather dressers whether East Indian tanned hides were being weighted by the Indian tanner, by the addition of mineral matter, or oil, more than was formerly the case. The flesh sides of many East Indian tanned hides, plastered over as they are with a mixture of a natural chalk, would certainly lead one to believe that these goods were being artificially weighted, and heavily so. With a view to ascertaining which particular tannages were the most heavily adulterated, a considerable number of analyses of samples obtained from a variety of different sources have been made.

The results of these are appended below.

TABLE I.—BANGALORE TANNAGES.

	A Pct.	B Pct.	C Pct.	D Pct.	E Pct.	F Pct.	G Pct.	H Pct.	I Pct.
Leather fiber	69.4	69.9	66.8	68.3	71.5	69.9	60.3	71.7	
Oil and fatty matter	8.2	11.5	9.4	9.4	7.2	8.5	17.9	6.3	10.2
Water soluble matter	9.4	6.9	9.7	9.1	8.9	8.1	10.4	8.0	11.3
Moisture	13.0	11.7	14.1	13.2	12.4	13.5	11.4	14.0	
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Mineral matter	1.1	1.8	1.6	1.9	0.4	2.0	1.1	0.5	

	J Pct.	K Pct.	L Pct.	M Pct.	N Pct.	O Pct.	P Pct.		Average Pct.
Leather fiber			72.1	70.4	61.2	63.8	71.8	(13)	68.86
Oil and fatty matter	7.2	3.6	6.0	8.3	7.2	7.5	6.5	(16)	8.43
Water soluble matter	6.7		7.6	6.4	5.9	14.2	6.9	(15)	8.6
Moisture			14.3	14.9	17.7	14.5	14.8	(13)	13.7
			100.0	100.0	100.0	100.0	100.0		
Mineral matter			0.9	0.9	0.7	1.6	0 4	(13)	1.12

It will be observed that in the case of this tannage, which is generally considered to be one of the primest of the East India imported leathers, that the amount of added oil and fatty matter varies from as low as 6 per cent. to as high as 17.9 per cent., though this latter is somewhat exceptional. The water soluble matter ranges from 5.9 per cent. to 14.2 per cent., though again this latter figure is much higher than the average. The water

* Tanners' Year Book, 1913, 165-9.

soluble in every case consisted of excess tanning matter and no sophistication with sugary matters was found to have taken place.

TABLE II.—MADRAS TANNAGES.

	A Pct.	B Pct.	C Pct.		Average Pct.
Leather fiber	70.2	72.7	65.1	(3)	69.33
Oil and fatty matter	10.3	2.9	13.3	(3)	8.83
Water soluble matter	6.3	7.3	6.7	(3)	6.76
Moisture	13.2	17.1	14.9	(3)	15.06
	100.0	100.0	100.0		
Mineral matter	7.1	0.8	1.2	(3)	3.03

TABLE III.—RANIPET TANNAGES.

	A Pct.	B Pct.	C Pct.	D	E		Average Pct.
Leather fiber	75.9	67.2	73.4			(3)	72.16
Oil and fatty matter	10.4	7.2	7.1	4.1	5.9	(5)	6.94
Water soluble matter	7.0	13.0	5.9	19.3		(4)	11.3
Moisture	6.7	12.6	13.6			(3)	10.96
	100.0	100.0	100.0				
Mineral matter	1.3	0.6	0.6			(3)	0.83

TABLE IV.—HYDERABAD TANNAGES.

	A Pct.	B	C Pct.		Average Pct.
Leather fiber	67.9		72.4	(2)	70.15
Oil and fatty matter	9.8	13.2	7.0	(3)	10.0
Water soluble matter	8.6		6.4	(2)	7.5
Moisture	13.7		14.2	(2)	13.95
	100.0		100.0		
Mineral matter	1.7		0.9	(2)	1.3

The Madras tannages were found to vary considerably more than others from different sources. One sample contained upwards of 7.1 per cent. mineral matter, and another no less than 13.3 per cent. of fatty matter.

TABLE V.—BOMBAY TANNAGES.

	A Pct.	B Pct.	C Pct.	D Pct.	E Pct.	F	G	H Pct.		Average Pct.
Leather fiber	78.4	76.4	75.8	76.6	75.6			76.8	(6)	77.6
Oil and fatty matter	2.3	5.1	7.2	4.8	4.6	3.7	4.8	7.3	(8)	4.97
Water soluble matter	5.6	6.6	3.4	4.9	6.6	6.9		5.0	(7)	5.55
Moisture	13.7	11.9	13.6	13.7	13.2			14.9	(6)	13.5
	100.0	100.0	100.0	100.0	100.0			100.0		
Mineral matter	1.2	4.3	5.8	0.6	0.9			2.3	(6)	2.51

The amounts of oil and fatty matter found in the above

samples range from as low as 2.3 per cent. to 7.3 per cent. The mineral matter which in three cases was as low as that found in the Bangalore tannages, was in two cases very much higher, these being cuttings from goods somewhat heavily plastered; and in some cases the water soluble matter was particularly low, showing the almost entire absence of loading by over-tanning. The leather fiber is the highest average of any of the various tannages analyzed.

TABLE VI.—COCONADA TANNAGES.

	A	B	C Pct.		Average Pct.
Leather fiber			73.9	(1)	73.9
Oil and fatty matter	10.9	5.8	3.8	(3)	6.83
Water soluble matter	6.5		5.3	(2)	5.9
Moisture			17.0	(1)	17.0
			100.0		
Mineral matter			0.5	(1)	0.5

Owing to the limited amount of the sample available for the purpose, it was only possible, except in one instance, to determine the oil and fatty matter present; this varied in the three samples from 3.8 per cent to 10.9 per cent.

TABLE VII.—COAST TANNAGES.

	A Pct.	B Pct.	C Pct.	D Pct.		Average Pct.
Leather fiber	66.8	73.4	65.9	73.7	(4)	69.95
Oil and fatty matter	8.9	5.6	12.1	5.0	(4)	7.9
Water soluble matter	10.7	7.7	6.6	5.2	(4)	7.55
Moisture	13.6	13.3	15.4	16.1	(4)	14.6
	100.0	100.0	100.0	100.0		
Mineral matter	1.2	0.8	0.8	0.7	(4)	0.87

The above are additional to the Madras tannages, and the results obtained are practically confirmatory of those given (with one exception), in Table 2.

TABLE VIII.—COLOMBO TANNAGES.

	A Pct.	B Pct.	C Pct.	D		Average Pct.
Leather fiber	76.3	76.9	71.2		(3)	74.8
Oil and fatty matter	2.9	5.1	7.8	3.6	(4)	4.85
Water soluble matter	4.6	4.3	5.7		(3)	4.86
Moisture	16.2	13.7	15.3		(3)	15.06
	100.0	100.0	100.0			
Mineral matter	0.6	0.5	0.5		(3)	0.53

These, with Bombay tannages, give the largest percentage of leather fiber; the amount of mineral matter is particularly low, and in two cases the amount of fatty matter is not more than would be found in a leather that had been simply oiled over for the purpose of protecting the grain surface whilst drying, and not with the idea of materially increasing its weight.

Three samples of Up Country tannages were analyzed for oil and fatty matter, and gave results as follows:—

A Pct.	B Pct.	C Pct.	Average Pct.
5.5	9.6	4.7	6.6

Two samples of tanned buffalo gave an average of leather fiber of 71.3 per cent., oil and fatty matter 7.6 per cent. moisture 13.7 per cent., water soluble matter 6.9 per cent., the ash and mineral matter found being 0.9 per cent.

TABLE IX.—MISCELLANEOUS TANNAGES.

	A Pct.	B Pct.	C Pct.	D Pct.	E Pct.	F	G	H Pct.		Average Pct.
Leather fiber	68.5	68.4	72.6	68.7	72.6			70.5	(6)	70.2
Oil and fatty matter	8.3	10.7	6.5	11.1	7.4	5.3	4.4	9.5	(8)	7.9
Water soluble matter	8.8	7.5	7.8	5.5	5.6	9.0		7.6	(7)	7.4
Moisture	14.4	13.4	13.1	14.7	14.4			12.4	(6)	13.73
	100.0	100.0	100.0	100.0	100 0			100.0		
Mineral matter	1.6	1.4	0.8	1.2	2.6			18.7	(6)	4.38

It would appear from the above analyses that adulteration of Indian tannages by the use of a large excess of oil and fatty matter, by use of mineral weighting matters, or an excess of tanning matter, was not nearly so common as one has been led to believe.

Whilst in many instances the amount of oil and fatty matter found is more than necessary to assist in obtaining a good colored leather by providing a film of oil to the grain side, except in a few cases the gain of weight obtained by the addition of oil is not nearly so large as one would have expected by a visual examination. The analyses compare very favorably indeed in the great majority of cases with the home tanned calf and dressing hides, and prove that adulteration is not general amongst this class of leather.

It has not been thought advisable to publish the origin of each particular sample, but as the names of the majority of the tanneries are known to me, I shall be glad to indicate the partic-

ular mark and tannery of any of the above samples to anyone who is interested and will apply to me privately for the information.

In conclusion I would like to record my indebtedness to Mr. Chas. Furneaux for carrying out the detailed analyses, and to Messrs. Flack, Chandler & Co., Culverwell Brooks & Co., Dyster, Nalder & Co., Malcolm Inglis., S. Barrow & Bro., Scriven Bros., and others who have supplied authentic samples.

THE GRAPHICAL METHOD OF RECORDING RESULTS.*

By J. R. Blockey.

The interesting paper of J. H. Russell in the JOURNAL OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION for August, 1911, on "Some of the Advantages of the Graphic Method of Recording Results in Routine Analyses," has induced the present writer to detail one or two instances in which the graphical method has been used with advantage for tannery control work, in the experimental tannery of the Leathersellers' Technical College.

Mr. Russell has described the method so well that only the instances and the conclusions need be given here.

The graphical method is simply a means of expressing figures by curves. Instead of having to wade through a mass of figures, and keep them in one's head, one discerns from a graph the whole significance and the relation of the figures to one another. It does not show anything which could not be gathered from the figures themselves, but it simplifies the process and renders possible, at one glance, what would otherwise take considerable time by a study of the figures.

To take the processes of the tannery in the order in which they are used, we will first consider the soaking process.

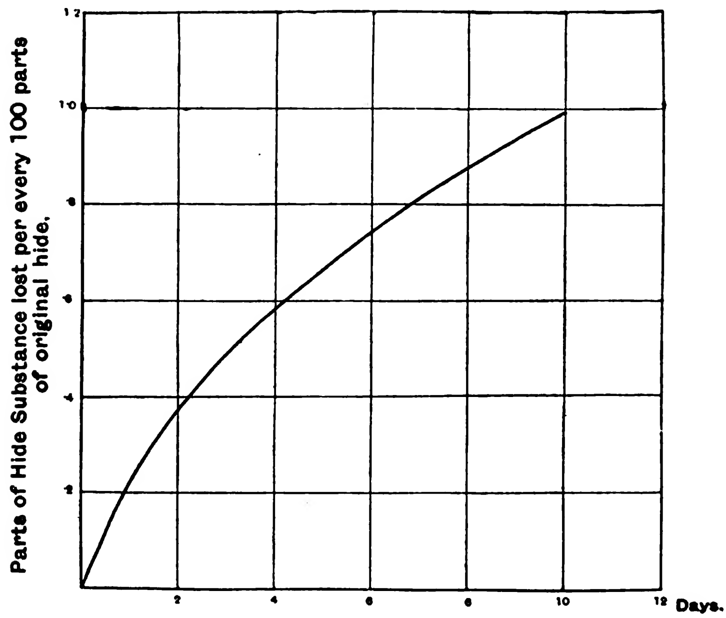
LOSS OF HIDE SUBSTANCE IN SOAKING AND LIMING.

One of the main things to consider, from the control point of view, is the loss of hide substance, but, as this is also one of the main items in the control of the liming process, the curves for the latter only will be given.

* Tanners' Year Book, 1913, pp. 103-11.

The following graph shows the amount of hide substance which is lost in the limes during the liming of a typical pack of hides for sole leather. It is needless to enlarge on the fact that, with leathers which are sold by weight, and with leathers which are required firm, the loss of hide substance should be as low as is consistent with the production of the right kind of leather, *e. g.*, in sole leather, the loss of hide substance should be as little as is possible, provided that the loosening of the hair, and the swelling

I. Curve showing the amount of Hide Substance lost in the liming of a pack of hides.



of the pelt are effected. The more the loss can be cut down the greater will be the yield of leather. Thus the determination of the amount of hide substance lost in the lime liquors is a very important factor in the control of the liming process.

The graph shows the amount of hide substance dissolved in the liming of a pack of hides for sole leather. The figures are obtained by the Kjeldahl method of nitrogen estimation, but, although this method gives quite accurately the total amount of nitrogen in the liquor, it does not differentiate between the nitro-

gen, which is due to the decomposition of the hide substance (leather forming substance) or merely to the decomposition products of the extraneous blood and filth, or even of the epidermis. On the abscissæ (*i.e.*, the horizontal lines) are plotted the number of days, and on the ordinates (the vertical lines) the amount of hide substance lost per every 100 parts of original hide.

This shows that the rate at which hide substance is lost, gradually diminishes with time. In the first three days, during which the hides were in a stale lime, nearly half the total amount of loss takes place, whereas, during the last four days, during which the hides were in a perfectly fresh lime, only half the amount of loss which takes place in the first three days occurs.

By drawing this curve for packs at different times of the year, evidence will be obtained as to the state and nature of the lime liquors. If the curve becomes steeper and reaches a higher limit, the limes being used are too stale, and should be replaced by fresher ones. It will be found that in summer the curve tends to become steeper, this is due to increased bacterial activity, and therefore the limes should be given fresher, or the length of time should be reduced.

Curves showing the increase in the amount of hide substance in the limes themselves are also instructive in the same way. They show the condition of the lime liquors, and if these be drawn at different periods of the year, the state of the limes can be regulated so as to make them as uniform as possible.

The following curve shows the amount of hide substance dissolved in a lime liquor which had been used in the "three pit" system, *i. e.*, it had been used (1) for four days as a fresh lime for a pack of hides which had already been in two other limes; (2) for three days as a medium lime for a pack which had been in one previous liquor, and (3) for three days as a stale lime for a fresh pack.

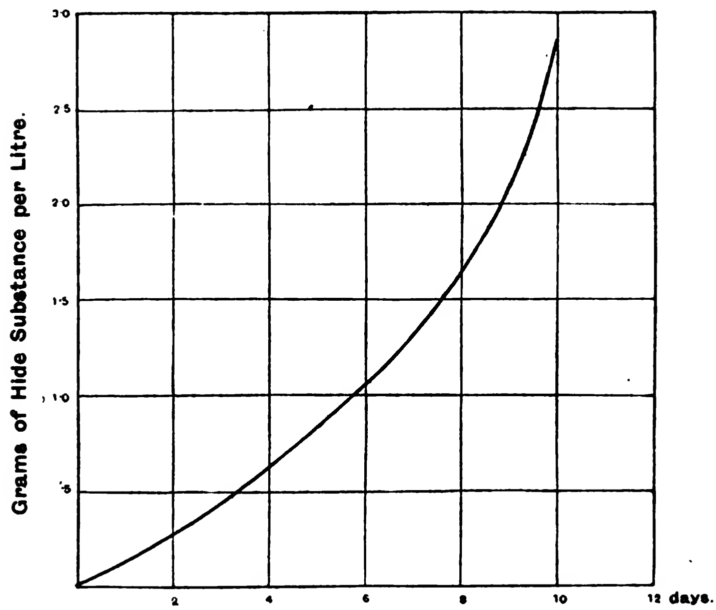
This shows that as the age of a lime liquor increases, its power of dissolving hide substances also increases, and the rate at which hide substance is lost is greater in an old lime than in a fresh one. By finding the lowest curve at which unhairing and plumping will take place, all other curves can be compared with

it, and so the condition of the limes may be kept at the lowest limit of freshness possible.

PENETRATION OF TAN IN LEATHER.

Another very interesting use of this method is to show the rate at which the tan penetrates the hide. By Kjeldahling the leather in every stage, from the moment it enters the weakest

II. Curve showing amount of Hide Substance during the ageing of a lime liquor.

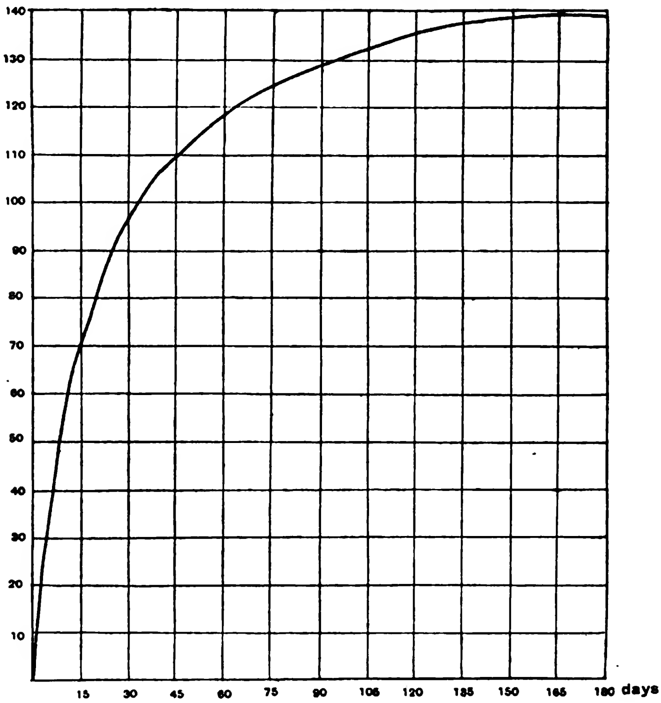


liquors to the time it leaves the last layer, the percentage of hide substance can be determined, and from this figure the tanning figure can be calculated. The tanning figure is the amount of tan which has combined with, or been taken up by 100 parts of original hide substance, and is of course a measure of the yield or rendement of leather produced.

The following graph shows the tanning figure for a typical pack of sole leather butts. On the abscissæ are plotted days, and on the ordinates the amount of tan taken up by 100 parts of hide substance.

This shows in a striking manner how rapid is the penetration of the tan in the first few days, and how the penetration gradually diminishes, until after about the 120th day there is practically no gain in weight at all. Perhaps it should be stated that this is for a mixed tannage, lasting three weeks in suspenders, five weeks in handlers, and about four months in layers; the strongest liquors being of a strength of 80° barkometer. It will be

III. Curve showing penetration of tan in Leather.



seen that half the total amount of tan is absorbed in the first 15-20 days.

Having once determined the speed at which the best results are obtained, the speed of tanning can be regulated by comparing the curves obtained.

The writer has recently seen some very instructive curves made on this plan in a large tannery. In one case a sudden drop in the curve revealed the fact that the liquor foreman had placed

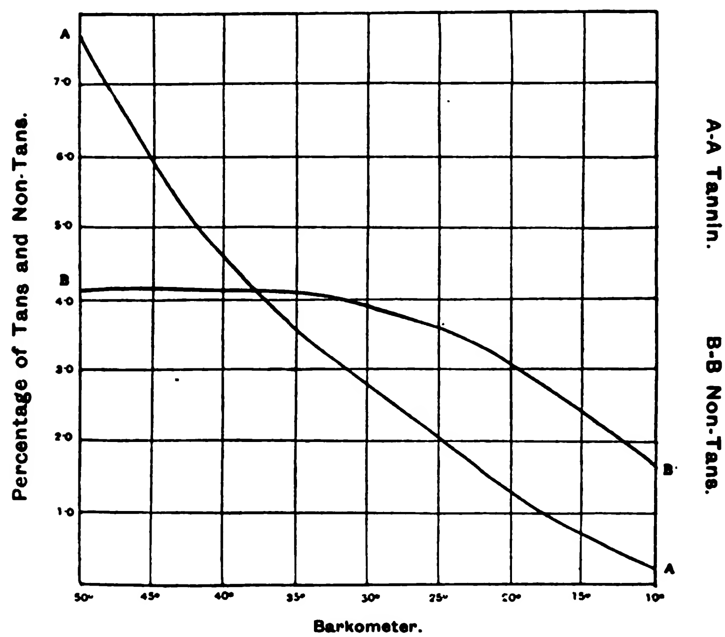
goods from a strong liquor into a weak one, and thus had actually reversed the tanning process. The effects of speeding up the tanning process, the use of new materials for making up the liquors, the increase in weight by hot-vatting can all be very clearly shown by this method.

COMPOSITION OF TAN LIQUORS.

The use of curves for showing the variation in the composi-

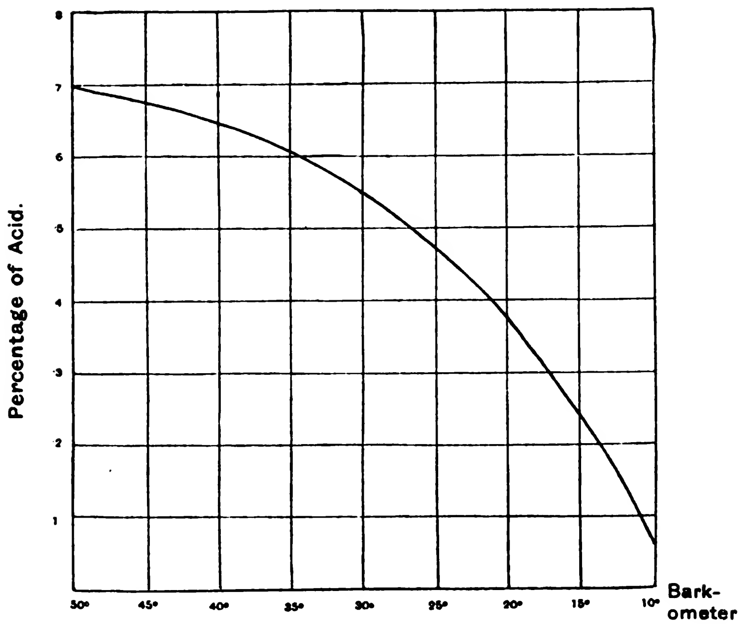
IV. A and B showing variation of tannin, non-tannin and acidity with the barkometer strength.

A

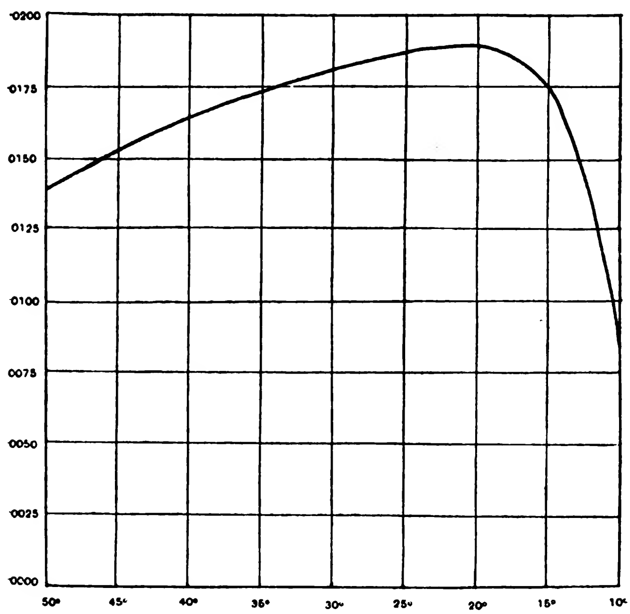


tion of tan liquors at different parts of the year, has already been described by Mr. Russell, but there is one feature which lends itself to graphical representation which he has not mentioned, and that is, the composition of the same liquor as it is worked "down the yard." This working down the yard means, that as the strong liquor made up for almost completely tanned leather becomes weaker, it is used for leather not so much tanned, and so on. As the liquor becomes weaker it is used for leather less and

B.


Percentage of Acid.
8
7
6
5
4
3
2
1
50°
45°
40°
35°
30°
25°
20°
15°
10°
Bark-
ometer

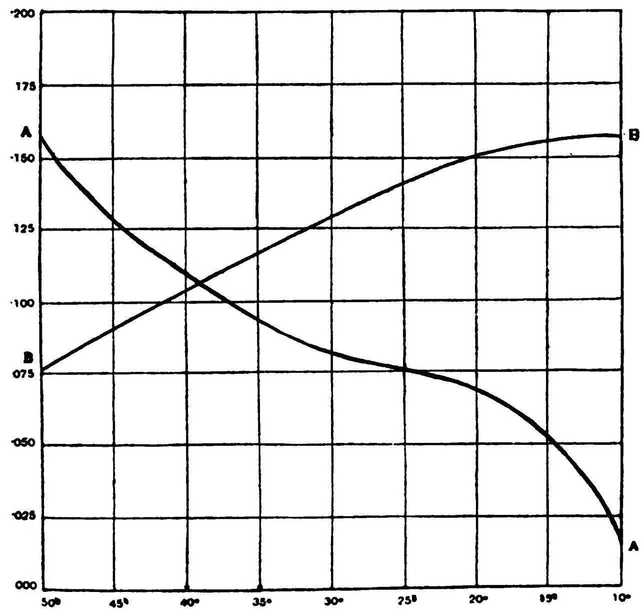
V.


·0200
·0175
·0150
·0125
·0100
·0075
·0050
·0025
·0000
50°
45°
40°
35°
30°
25°
20°
15°
10°

less tanned, until it is almost completely expended, when it is used for the raw pelt. In the experimental tanyard at the Leathersellers' Technical College this plan is adopted. Liquors from the layers go to the top handler, at 50° barkometer and then gradually pass down the yard until they are ready for throwing away.

The graphs IVa and IVb show the variation of tannin, non-tannin strength, and acidity, with the barkometer strength.

VI.



The tannin strength gradually diminishes, almost to vanishing point; diminishing more rapidly at first than later. The non-tannin strength remains almost constant for a considerable time and then gradually diminishes, but of course never to zero. One reason why the tannin diminishes more rapidly than the non-tannins is probably that whilst some of the tannin which disappears is absorbed by the leather, others of it is decomposed into non-tannin matters, so that as non-tannin matter is absorbed by the leather, more is being formed at the expense of the tannin,

and therefore, the amount of non-tannin in the liquor does not rapidly diminish. When it does begin to diminish, it probably is decomposed into acid. That this is probable is shown by the fact, that the amount of acid in the liquors is relatively highest at the point when the non-tannins begin to diminish rapidly. For convenience the acidity curve is drawn to a different scale to that of the tan and non-tannin curves, and is reckoned as acetic acid.

A better way of representing the variation of tannin, non-tannin, acidity, etc., with barkometer strength, is to plot the barkometer strength against the figures obtained by dividing the percentages of tan, etc., by the barkometer strength. This method shows the points at which the relative amounts of the different constituents are highest. Figure V. shows the curve thus obtained by plotting the barkometer strength against the figures obtained by dividing the acidity by the barkometer degrees.

It will be seen that this ratio is highest when the barkometer is at about 20 degrees, or at the same point at which the non-tans begin to diminish rapidly.

Figure VI. shows the same for the tannins and the non-tannins.

SAMPLING OF LIQUID TANNING EXTRACTS FOR ANLAYSIS.*

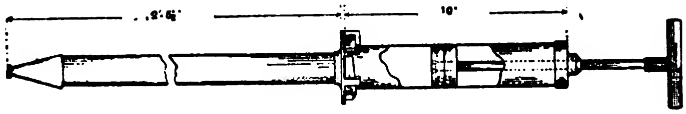
By Andrew Turnbull.

In the *Tanners' Year Book,* 1905, page 76, I described and recommended a tool for drawing samples of liquid extracts. After considerable experience I found that although this instrument when properly used answered all ordinary requirements, it was quite useless for obtaining separate samples from individual casks, and for sampling the thick extracts which are so much in favor at the present time.

I have now designed an instrument which I find answers every requirement. This consists of a brass syringe 10 inches long, and 1⅞ inches bore with 8¾ inches stroke. The piston is of ⅜ inch rod secured by a nut to two cup leathers placed back to back. A brass tube, 2 feet, 5½ inches long and 1⅜ inches wide has a

* Tanner's Year Book 1913, pp. 112–13.

bayonet coupling at one end which can be tightly fitted with a thin rubber washer to a bayonet lock coupling fixed on one end of the syringe. This tube has a brass nozzle at the other end bored ⅜ inch for sampling thick liquids, and taking a loose brass plug bored ¼ inch for thin liquids.



When sampling I take a number of casks equal to the square root of the total number of casks in the delivery, choosing the numbers as widely apart as possible. The bungs are removed, and with a Malacca cane 4 feet long and 1 inch thick the contents of each cask is thoroughly stirred, working the cane vigorously along the sides and into the corners of the casks. The tube is connected with the syringe and put into the cask so that the nozzle is about four inches from the bottom. Fully half-a-pint of the extract is sucked into the tube from each of the selected casks, and discharged into a papier-mache bucket, where it is well stirred with the cane, and then transferred by means of the instrument to clean dry 8-ounce bottles.

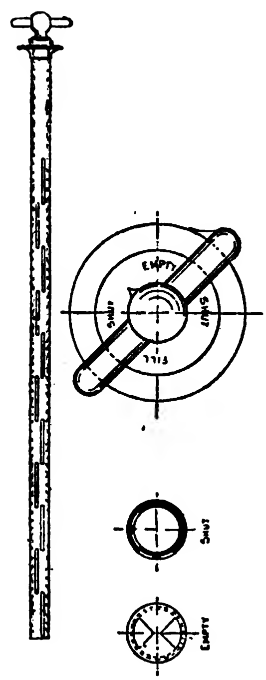
The cost of the sampling-tool is 30/-

[We add the following from the *Leather World*, describing an instrument which seems well adapted for sampling liquid extract, although intended for use in sampling drums of glycerine.—Ed.]

The usual method of sampling has hitherto been by means of a glass tube, which is slowly lowered into the drum with the object of taking as nearly as possible a vertical section of the glycerine contained in the drum. This method has been found unsatisfactory, owing to the fact that in cold climates viscous glycerines run into the tube very slowly, so, owing to the time occupied, it is impossible to take a complete section of the sample. Another objection to the glass tube is that it fails to take anything approaching a correct proportion of any settled salt contained in the drum.

The sampler which is illustrated herewith has been devised with the object of overcoming the objections to the glass tube as

far as possible. It consists of two brass tubes, one fitting closely inside the other. A number of ports are cut out in each tube in such a way that when the ports are opened a continuous slot is formed which enables a complete section to be taken throughout the entire length of the drum. By this arrangement the glycerine fills into the sampler almost instantaneously. There are also a number of ports cut at the bottom of the sampler which render



it possible to take a proportion of the salt at the bottom of the drum. The instrument is so constructed that all the ports, including the bottom ones, can be closed simultaneously by the simple action of turning the handle at the top; a pointer is arranged which indicates on a dial when the sampler is open or closed. In samplers of larger section (1 inch) it is possible to arrange a third motion whereby the bottom ports only are open for emptying, but in samplers of smaller dimensions (⅝ inch)

this third motion must be dispensed with, otherwise the dimensions of the ports have to be so small that the sampler would not be efficient.

In using the sampler it is introduced into the drum with the ports closed, and when it has touched the bottom the ports are opened for a second or two, then closed and withdrawn, and the sample discharged into the receiving vessel by opening the ports. When the drum contains suspended salts the ports must be opened before the sampler is pushed through the salt, thus enabling a portion to be included in the sample. It is, however, almost impossible to obtain a correct proportion of salt after it has settled in the drum; it is therefore recommended that the drum should be sampled before the salt has settled.

A sampler 1 inch in diameter withdraws approximately 10 ounces from a 10 cwt. drum.

A sampler ⅝ inch in diameter withdraws approximately five ounces from a 10 cwt. drum.

NERADOL D AND ITS PRACTICAL APPLICATIONS.*

Address at the meeting of the German Section, I. A. L. T. C., June 22, 1913.

By H. Dierdorf.

Gentlemen:—I have been commissioned by the Badische Anilin und Soda Fabrik in Ludwigshafen a. Rhein to give you an account of Neradol D and its practical uses, as far as our experience allows.

Those members of the I. A. L. T. C. who have not yet had opportunity personally to use Neradol D, are yet not quite unacquainted with it since Professor Stiasny on March 8th last gave a lecture on Neradol D before the British Section of the I. A. L. T. C. (*Collegium*, 516).

It was Professor Stiasny who first found a method suitable for industrial use, for making synthetic, soluble products, which in important respects correspond to vegetable tannins. He thus gave the first impetus to the investigation of this important field.

* *Collegium*. 1913 p. 266-74 July. Translated for J. A. L. C. A.

The *Collegium* has already printed sufficient information about the chemical character of Neradol D. With the synthetic tanning material already discovered it is a question of formaldehyde condensation product of sulphonated phenol which Prof. Stiasny named Syntan. The product under discussion is such a Syntan, which the Badische Anilin und Soda Fabrik puts on the market under the name of Nerodol D.

This is produced in pasty form, as you will see by the sample I hand around, and it reminds one outwardly of vegetable tanning extract.

Neradol D is slightly acid and easily forms a perfectly clear semi-colloid solution in cold water, which gives precipitates with gelatin solution, lead salts, anilin hydrochloride, etc. Like vegetable tanning materials it has the power to change white hides into very good useful leather. Neradol D solutions as well as leather tanned with Neradol D when treated with iron salts also give the deep blue-black color characteristic of vegetable-tanned leather.

The analyst will next wish to know how much tanning material is present in Neradol D. According to the usual hide powder method apparently about 32 per cent. tanning material is determined. It is further to be observed that this synthetic tanning material is not of identical constitution with the natural tannins, so they behave differently and less Neradol D is used to convert white hides into leather than of natural materials of like or higher tannin content. It follows that the tanning power of Neradol D seems much higher than one would expect, judging by the usual methods of analyzing natural tannins. Thus it will be necessary to work out a special method for these synthetic tannins which will do justice to its real tanning value.

The gravimetric determination of the tannin content of Neradol D also gives differing results with the usual hide powder method and also with like substance, test and method of work, since the determination of total solids as described above by drying at 100° C. or 105°-110° C., easily leads to carbonization and thus to irregularities. Carbonization of Neradol D can be fully prevented if the drying is carried on at 45° to 50° C. in a vacuum

drying oven. Under these circumstances we have always obtained uniform results for the total solids.

I should like also to point out, at this time that Neradol D may be precipitated according to the well known Procter-Hirst method with anilin hydrochloride, and that, although it contains no trace of lignin, yet it gives the same reaction as the waste liquors of paper pulp manufacture so much discussed on account of their tanning value.

Since the Procter-Hirst anilin reaction is still generally considered typical for the recognition of sulphite-cellulose extract, it seemed very expedient to find a reaction which would make it possible to differentiate sharply between Neradol D and sulphite cellulose extract, and also to detect possible mixtures of the two. This reaction has been found by Prof. Stiasny and already published by him (*Collegium,* 516).

I quote the following:

"To tell the difference between Neradol D and sulphite cellulose, and to detect the latter when mixed with Neradol D the following reaction may be recommended: 10 cc. of a 5 per cent. solution of the extract in question is thoroughly shaken up with 1 or 2 drops of one per cent. alum solution and about 5 grams of solid ammonium acetate. In the presence of pure Neradol D the solution stays clear even after standing 24 hours, while sulphite cellulose extract gives a heavy, flaky precipitate, which appears in mixtures all the more quickly the more sulphite cellulose there is in them. With a content of 5 to 10 per cent. a very noticeable precipitate appears after 2 or 3 hours. If the solution is clear after standing over night one may conclude that there is no sulphite cellulose in it."

If we now consider leather made with Neradol D and no other tanning material we are surprised by the almost white color. This surpasses in purity of shade even tanning with bleached Sumach extract. There is no vegetable tannin which produces a leather of a pure shade like Neradol D leather.

The structure of Neradol D leather is very tough and long fibered, but on the other hand this synthetic tannin lacks filling action. For this reason pure Neradol D tanning is only used on light leathers and perhaps in special cases in question where no

importance is placed on filled leather. Where filling action is demanded, that is with all heavy leathers, Neradol D can probably be used only up to a certain per cent. composition, whether it is used together with other tanning material or alone for preliminary tannage. I shall say more of this later. The best leather for pure Neradol D tannage, as before mentioned is light leather—for example split sheepskins or lighter sheep and goatskins. I will show you a few samples of that kind of Neradol D leather which were made in actual practice.

Further you see here a sample of pure Neradol D tanned cowhide, which is merely to show that Neradol D is quite capable of completely tanning thicker hides too. This sample was for example tanned in 4 days in the laboratory, merely by hanging the white hide in a Neradol D liquor of 2° Baumé. It contains no stuffing and was dried without special care after slight rinsing and stretching. The softness and white color are astonishing.

As you all see by these samples, the color is not only beautiful, but the leather itself is also quite tough, and there is no doubt that light leather tanned with Neradol D would be easily salable.

Tannage of light leathers proceeds very easily and smoothly and is like the usual method with sumac or bleached sumac extract.

A short time ago I tanned several goat and sheepskins, together in a drum or paddle. The hides were delimed beforehand as usual and then bated with Oropon. For tanning, nearly 10 kilos Neradol D were used to 100 kilos of hides. After 3 hours of drumming a second installment of 10 kilos of Neradol D was added and after 3 more hours of drumming the sheepskins were almost tanned through. Since the goatskins were slightly less tanned 7 kilos more of Neradol D was put in, and after 3 additional hours the whole batch was thoroughly tanned. Thus the total duration of the tanning was 9 hours and 27 kilos of Neradol D were used to 100 kilos of hide. [Samples of this leather were shown]. This sample is also entirely unstuffed. A part of this batch was colored and finished (sample shown) and the softness and finish of the leather met with the full approval of the concern which manufactured it. This sample proves that Neradol D tanned leather

can be colored if the right dye is chosen, and that it can be perfectly finished. This can also be observed by looking at the piece shown you, which was finished for hat linings, and is undyed. It was tanned in England with Neradol D.

If the leather is to be fat-liquored in the vat it is best to use a neutral or slightly acid oil, for alkaline solutions are liable to partly de-tan the Neradol D leather.

Further experiments on a larger scale have been made with heavier sheepskins which generally take 50 per cent. of quebracho-extract for complete tannage. A larger amount of Neradol D was used than before and the tanning carried on in the usual manner in drums.

To begin with 3 per cent. of Neradol D was used in this case—reckoned on the weight of the white hide—for preliminary tannage in the drum. After an hour the same bath was strengthened with a mixture of 2 parts quebracho extract and one part Neradol D, and several hours later strengthened again with the same mixture. The tanning was finished in 24 hours, and the result very satisfactory. To 100 kilos white hide, 18 kilos quebracho extract and 12 kilos Neradol D (including the preliminary tanning with Neradol D). [Sample shown.] A sample of sheepskin, slightly tanned beforehand with Neradol D and chestnut extract and finished with Neradol D alone might interest you. [Sample shown.]

Neradol D, instead of finding its most important use in tanning lighter leathers alone, seems destined to play a large rôle in the heavy leather industry, especially when used in combination with the usual vegetable tanning material. Neradol D possesses qualities which make it possible to shorten appreciably the otherwise long tanning process with vegetable tannins in the heavy leather industry.

Preliminary tannage, combination tannage or after tannage with Neradol D result in a very tough, indestructible leather. This so far surpasses leather tanned without it that practical men believe that a suitable combination of Neradol D can make a great improvement in the quality of sole-leather.

The lighter color of the finished leather which can be obtained by combination use of Neradol D is very noteworthy. The

brightening action is attained as well by simple preliminary tannage with Neradol D as by an addition of it at the end of the process, when it works like a bleach.

If Neradol D is used together with natural tannins in the same series of rockers, the brightening of the leather is naturally, accompanied not only on the outer surfaces, but also in the cross-section. In cases where this is not desired it is best to use Neradol D only as preliminary tannin.

There are, therefore, as you well have gathered, three possible uses of Neradol D for heavy leathers like sole leather, vache leather, strap leather, trunk leather, etc.

1. *Preparatory tanning.*—The work is carried on as usual hanging well delimed and bated white hides in a 1° Baumé solution made from about 25 kilos Neradol D to 1,000 liters of water, from 12 to 24 hours. Then the skins thus well tanned in a preparatory manner with Neradol D are put through the regular series of vats with the usual tannins. In this connection experience has shown that white hides thus tanned beforehand with Neradol D, show a surprising affinity for the tanning substance in the subsequent baths, as they absorb the tannin from the vats much more quickly than those hides put in without being treated with Neradol D. It has also been shown that hides thus treated can be put immediately into stronger liquors without fear of drawing grain or stiffness. If there is nothing in local conditions to hinder, it seems to me possible, for example, in a six vat series to put the hides treated with Neradol D into the usual second, and next into the fourth vat, and after that into the fifth and sixth. Also the usually thin first vat can be brought to 1° or 2° Baumé with Neradol D and this first vat thus used as a preliminary tanning bath.

If a separate preliminary bath is installed (as described above) this can be used quite a long time if the hides are carefully delimed and bated before putting them in. I had opportunity to see a sole leather tannery which had already used one and the same Neradol D preliminary bath regularly for many weeks. It needs once in a while just a proportionately small addition of Neradol D to bring the bath up to 1° Baumé again, with each addition. In a northern tannery great advance has been

made toward another method of work, on light weight leather, after preliminary experiments had given good results on a small scale. Here Neradol D is used up to complete tannage in liquors gradually strengthened up to 10° Baumé for 8 days. Then the hides were placed in a vegetable bath of about 6° Baumé and then in extract. (Sample shown). The leather was not rinsed and not finished but dried as it was without care. The color and flexibility of it are particularly striking.

Neradol D cannot of course be used for plumping material, as was first understood in isolated districts. When the hides are put into a preparatory bath of Neradol D (1-2° Baumé) a very slight swelling is noticeable during the first few hours, but it soon ceases.

I should like to show you a few experiments on cowhide which illustrate very well the brightening action of Neradol D preparatory tannage. They were made in the laboratory on a small scale in handlers. They tanned in a preliminary way a few rather large samples of well delimed white hide at first with a 15 hour treatment in a Neradol D liquor of 1° Baumé, then these prepared samples were completely tanned in liquors together with samples of the same cowhide which had not been previously treated. These were put in with oak extract, chestnut, cold soluble quebracho, solid difficultly soluble quebracho, sumac extract and gambier, as commercially obtainable. The length of the process was 9 days, then the samples were well washed, stretched, and then thoroughly oiled on the outside with mineral oil. The results may be seen by these samples, which I pass around.

The striking action of Neradol D, preliminary tannage is everywhere recognizable, and is astonishing with many extracts, such as quebracho and gambier.

2. *Use of Neradol D with Vegetable Tannins.*—This method would be used mostly when for certain local reasons preparatory tannage is impossible. In this case 0.25 to 0.5 kilos Neradol D, reckoned on 100 kilos white hide, is added to the usual series of rockers. In the subsequent complete tannage in the drum Neradol D can likewise be added, but it has been found best not to exceed a total addition of five kilos of Neradol D, that is

inclusive of the quantities added in the handlers. If more Neradol D is added the leather becomes much too soft for use as sole leather, for instance. From this fact it is on the other hand apparent that in special cases where a greater softness in heavy leather is desired, it can be attained by using larger quantities of Neradol D.

This use of Neradol D together with other tanning materials has, as with other methods, a very good effect on the toughness of the leather, and on the color of the finished product. Now I should like to show you samples of sole leather one of which was tanned as usual without Neradol D, the other produced by a combination of Neradol D, but with the same tanning material and by the same process. The leather is not only lighter in color, but above all much tougher and more pliable.

3. *Neradol D as Bleach.*—It is well known that in consequence of the strong tanning extracts and the darkening incident to drying most heavy sole leathers must be bleached. This is done as a rule by using strong alkalies and organic or inorganic acids, which of course harm the quality of the leather and make it brittle, and besides the process involved is usually quite fussy and time-consuming.

In these cases a subsequent treatment of the finished leather with Neradol D offers great advantages over the former bleaching methods. It not only gives a very good bleach effect but also insures no loss of tanning material and the leather is subjected at the same time to after tannage which improves the quality. The best method is to put the hides to be bleached in a solution of about 50 gr. Neradol D in a liter of water *i. e.*, 2° Baumé for a few hours, possibly over night. Where local conditions render this method impossible the leather to be bleached can be put in a drum for 2 or 3 hours with 3 to 5 per cent. Neradol D —reckoned on the weight of the leather,—and not too much water.

Successful results have already been obtained in bleaching sole leather by thoroughly brushing the finished hides with a 4° Baumé solution of Neradol D, whereby all loss of weight is of course avoided. The brush liquid can be strengthened to 8° Baumé; but it has then proved advisable to brush it afterwards with warm water when the bleach is better.

In isolated cases the observation was made that leather treated with Neradol D in the rockers, to bleach it, turned still darker when it was dried and was more brittle. In this case the hides were those which had been tanned with strong extracts, partly difficult of solution, and which were taken right from the extract tannage and put immediately without any further treatment, into the Neradol D bath. In this case an undesired but nevertheless valuable characteristic of Neradol D came to light. This is that the Neradol D acted as a strong solvent on the difficultly soluble parts of the extracts used in completing the tannage. Thus in the bleach bath, a further immediate after tannage of the grain or outsides of the hides took place, by means of the parts of the other vegetable extracts which were becoming soluble. And this caused the appearance of the darkness and brittleness of the fiber, which was complained of. This disadvantage could be largely removed by subsequently washing off the leather, when the desired brightening comes out.

There is still another use of Neradol D to be mentioned, which is used with excellent results in the trade on heavy strap leathers. The last tanning is followed by a rinse water in the vat to which a certain per cent. of Neradol D is added. The result obtained was pointed out to me in the tannery in question as exceptionally favorable. The other tannins were made firmer by this after bath of Neradol D, as was convincingly shown later in the output of the leather, and it was also shown that a slightly higher rendement could be observed. Further the color of the finished leather was very beautiful, and fas superior to the leather produced before without this after-wash.

The Neradol D wash water, in which a part of the other tannins, merely adhering to the surface was dissolved, and in place of which part of the Neradol D went into the leather, is used again in the handlers.

I will show you a few cowhide samples which will make clear to you the bleaching action of Neradol D. They were tanned in the laboratory, with preparatory tannage in handlers. A different vegetable tannin was used for each one—oak, chestnut, cold-soluble quebracho, solid difficultly soluble quebracho, and sumac extract, as well as gambier. After the tanning bath and thorough

draining a part of the leather was rocked 6 hours in a bath of $1°$ Baumé Neradol D, then rinsed a little and lightly rubbed with a mineral oil. As you can see the bleaching, in comparison with that not tanned with Neradol D, is very striking.

I should now like to refer to the important observation, that in all cases where heavy leathers are treated with Neradol D in any of the above-mentioned ways, they take up more fat than those hides tanned without Neradol D. This can be without doubt regarded as a further advantage in the use of Neradol D.

It is to be expected when the tanning industry has become well acquainted with the characteristics and advantages of Neradol D, that a way will be found of cheapening the cost of tanning without affecting the high quality of the leather. This might be, for example by mixing Neradol D with larger quantities of such tanning materials as have heretofore been out of use for certain reasons such as a poor color.

While a wide field is open for the use of Neradol D in the production of vegetable tanned leather, yet it ought also to find important use in the production of cold-soluble tanning extracts of vegetable origin. As I have before mentioned Neradol D is surprisingly effective in dissolving the difficultly soluble parts of vegetable extracts, particularly in impure quebracho. The solubility of the latter varies with its origin. I have seen unsulphited quebracho extracts from which good cold-soluble extracts could be obtained by merely mixing with warm Neradol D, without long boiling. They have already had analyses of difficultly soluble tannins in connection with Neradol D, whose figures showed an increase in value in that kind of extracts. But we have as yet no results taken from actual practice, which will disclose what relation these figures bear to the tanning value, that it, whether leather treated with these extracts will turn out correspondingly better in quality.

The experiments in the use of synthetic tanning materials for rendering extracts cold soluble, are (as mentioned above) not yet concluded, but promise very pleasing results.

As you will have gathered from my short remarks the Badische Anilin und Soda Fabrik has opened a new field in taking up the manufacture of the synthetic tanning materials, and in introducing

them into practical tanning. As with all fundamentally new undertakings the introduction of Neradol D will from time to time offer difficulties to be studied and prejudices to be overcome. But the fact that the excellent characteristics of Neradol D are already so widely recognized after so short a time, and that its introduction makes such satisfactory progress, allows us to hope that this new synthetic tanning material will soon have gained its rightful place in the tanning world.

NERADOL D.*

By Georg Grasser.

The problem of the synthesis of tannins has made progress of recent years largely through the work of Emil Fischer. The fruits of these purely scientific researches would, however, be likely to remain for a long time unavailable to the technician, since the complicated syntheses involved have not been reduced to a form practicable for wholesale production. It was therefore of special interests to science and technical circles alike to learn that Stiasny had succeeded in preparing by a very simple process substances which showed not only extensive analogies with the natural tan-stuffs, but also surprising results in relation to tanning power and practical value.

The Badische Anilin und Soda Fabrik undertook the commercial production and distribution of the new products, and at the end of a year's work on the project are able to show a tanning material of high technical excellence. Many ways were worked out of producing such substances, having tanning properties, the particulars of which are detailed in the published patents. The materials which result are representatives of the group of formaldehyde condensation products of sulphonated phenol, which have been partially neutralized. Although the chemical reaction of this condensation appears somewhat simple, the fact that the chemical constitution of these compounds has remained thus far unknown may be explained by the observation that the

* *Collegium*, 1913, pp. 413-16. Translated for the Journal of the American Leather Chemists Association.

only condensation products of these substances heretofore prepared, (Bakelite), are insoluble in water.

The above-named factory has already produced and placed on the market in wholesale quantities a product which they have named Neradol D, which is in the form of a heavy liquid or paste of about 40° Baumé, and in appearance reminds one of a vegetable tanning extract. Of special technical importance is its ready solubility in water, in which it makes a clear solution of a semi-colloid character.

The reactions of this water solution are as follows: methyl-orange, red coloration; barium chloride, heavy precipitate, insoluble in nitric acid; copper sulphate, no reaction; ammoniacal copper sulphate, red-brown precipitate, soluble in excess of the precipitant to a deep brown solution; ammonia, no reaction; ferric chloride, deep blue color; lead acetate, white precipitate; gelatin, flocculent precipitate; anilin hydrochloride, heavy white precipitate; basic anilin dye, precipitate; no reaction with bromine water, formalydehyde and hydrochloric acid, zinc acetate, crystals of sodium sulphite, lime water or iodine water. These reactions show the great similarity of Neradol D to real tannin. The only notable differences are its behavior toward formaldehyde and hydrochloric acid and toward bromine water. The lack of any iodine absorption which shows the absence of unsaturated compounds explains the important property of Neradol D of not darkening in the air by oxidation.

Another exception is the reaction with anilin hydrochloride, which gives a precipitate, (Procter-Hirst reaction for sulphite-cellulose) in spite of the absence of any trace of lignin or any cellulose-like substance. In order to distinguish between Neradol D and sulphite-cellulose in extracts, Professor Stiasny has worked out the following test: 10 cc. of a 5 per cent. solution of the extract to be tested is vigorously shaken with 1 or 2 drops of a 1 per cent. solution of alum and about 5 grams of solid ammonium acetate. Pure Neradol D remains clear on standing 24 hours, while sulphite-cellulose gives a heavy flocculent precipitate, which is heavier in proportion to the amount of sulphite-cellulose present. From 5 to 10 per cent of the latter gives a distinct precipitate after 2 to 3 hours' standing.

When after standing over night the solution is clear, the absence of sulphite-cellulose is proved.

On cooling to 8° C., Neradol D deposits many needle-shaped crystals of sodium sulphate, formed in the partial neutralization of the product, and which check the otherwise too energetic tanning action of pure Neradol D. The presence of free swelling acids favors the usefulness of Neradol D in the early stages of tanning. A used handler liquor containing Neradol D which has been nearly neutralized by the lime, etc., carried in by the hide, so as to be almost useless, may have its original content of sulpho-acids restored by suitable acidification with organic acids.

Neradol D is insoluble in the following organic solvents: ether, carbon disulphide, chloroform, carbon terachloride, epichlorhydrin, amyl alcohol, acetone and benzol. In alcohol, glacial acetic acid and acetic ether, it is soluble, except its inorganic constituents.

A quantitative analysis gave the following, (shake method):

	Per cent.
Water	34.5
Tanning substance	32 5
Soluble non-tannins	33.0
Insolubles	0.0
Ash (Na_2SO_4)	17.4

Hide treated with pure Neradol D gives a leather almost pure white, similar to alum-tanned leather. Chrome leather is apparently not influenced, at least treatment with Neradol D does not change its blue-green color.

Neradol D mixes with vegetable tan-liquors without precipitation of the vegetable tannin. It may therefore be used in admixture with any vegetable liquor without loss of tannin, differing in this respect from sulphite-cellulose. Although a recent patent offers and recommends the latter for rendering quebracho extract soluble, reference to the experiments of Yocum and Faust* shows that the addition of sulphite-cellulose to vegetable tanning extracts causes insolubles to separate, thus diminishing the amount of soluble tannin, except in the case of quebracho. If, therefore, a quebracho extract made soluble by the use of sulphite cellulose were used, when the liquors were

* Journal A. L. C. A., VI, 537-43.

strengthened by addition of other tannins, this precipitating effect of the sulphite-cellulose would come into play. Addition of from 15 to 20 per cent of Neradol D to a liquid quebracho extract which has been treated with sodium sulphite gives a cold-soluble product.

Among other applications of Neradol D, its facility in rapid fore-tannage is especially conspicuous. Either upper or sole leather treated with a liquor of Neradol D of a strength of four to 5° barkometer, or with a vegetable liquor to which Neradol D has been added, will have its time in the fore-tannage reduced by a third. Care must be taken not to have the first liquor, if of pure Neradol D, stronger than 5°, or if it is a mixture, the amount of Neradol D must not be more than enough to make a liquor of 5°. Otherwise the tanning will proceed too energetically, and draw grain and "dead" tannage will result. For example, if one is accustomed to give upper leather a fore-tannage consisting of 2 days each in liquors of 4, 6, 8, 10, 14, 20, 26 and 30 degrees barkometer, as good results will be obtained if for the above series be substituted 2 days each in liquors containing Neradol D, whose strengths are 5, 14, 21° and 30°, a total of 8 days.

Neradol D may also be used to great advantage as a bleaching material. A liquor of pure Neradol D of 8° Baumé is brushed over the surface of the leather to be bleached. Instead of a loss of weight, there is a gain due to the Neradol D used. Leather made with Neradol D is not only brighter in color than that made without it, but has notably tougher fiber, as is shown by tests of its resistance to tearing.

In the analysis of leather tanned with Neradol D, it will be found that the ash content is high, and also that of sulphuric acid. The latter is due to the splitting up by heat of organic compounds containing sulphur that were in the Neradol D, and therefore it has no injurious effect on the fiber, as is shown by the high resistance of the leather to tearing.

A thorough working out of the properties of Neradol D, and of leather tanned with it, will yield valuable results, and will contribute to bring this new product rapidly into general use, as it deserves.

BOOK NOTICE.

Manuale del Conciatore. Dr. Augusto Gansser. Milan; Ulrico Hoepli. Dr. Gansser's Tanners' Manual is a very attractively gotten up little book. It has 382+24 pages, 3 13/16 by 5 3/4 inches in size, with rounded corners. It is bound in flexible leather of a very light shade of tan. The price is 4.50 lire, equivalent to about 90 cents.

The type is about the same size as that in which the abstracts in this Journal are printed. There are many illustrations, chiefly of machinery. The chapter titles, and number of pages devoted to each subject, are as follows: I. Leather. 5. II. The hide and its properties. 6. III. Defects and damages in the Hide 28. IV. Water for the Tannery. 6. V. Preparation of the Hide for Tanning. 35. VI. Tanning Materials. 33. VII. Transformation of the Hide into Leather. 21. VIII. Substances used in finishing Leather. 13. IX. Finishing Processes. 12. X. Various Treatments of Tanned Skins. 18. XI. Stuffing of Leather. 7. XII. Adulteration of Leather. 9. XIII. Bleaching of Leather and Skins. 4. XIV. Dyeing of Skins. 17. XV. Vegetable Tannage. 42. XVI. Alum Tannage. 8. XVII. Oil Tannage. 6. XVIII. Combination Alum and Vegetable Tannage. 5. XIX. Formaldehyde and Quinone Tannages. 7. XX. Mineral Tannage. 6. XXI. Chrome Leather and its properties. 33. XXII. Combined Mineral and Vegetable Tannage. 5. XXIII. Tanning Action of Various Substances. 2. XXIV. Purification of Hard Water in the Tannery. 5. XXV. Analysis of Tanning Materials. 10. XXVI. Analysis of Leather. 12. XXVII. Rendement. In the Appendix are directions for treatment in case of anthrax infection, some general advices to the tanner, and tables of various sorts, including comparison of Centigrade and other thermometer scales, and comparison of various hydrometer scales.

ABSTRACTS.

A New Unhairing Process. DR. OTTO RÖHM. *Collegium,* 1913, 374-377. After Dr. Röhm had succeeded, by means of his Oropon bate in excluding bacteria from the bate process and using only the enzymes, he made further investigations to see whether the same principle could not be employed in the unhairing process.

It also seemed to him desirable to exclude caustic lime from the process, although it has been considered indispensible. But in combination with the hardness of the water or with the carbonic acid gas of the air it causes lime stains on the white hides which lessen the value of leather especially for dyeing. The tanner who has soft water is not troubled with lime stains, but hard water is usually the only kind to be had. It also seemed important to exclude the sulphides which destroy hair and wool, damage glue stock and contaminate waste water.

In December 1910 it was found that skins can be unhaired and at the same time kept stainless if they are treated for a few days with an alkaline tryptase solution. Here the way opened to produce a clean white hide without bacteria, sulphides or bates. This principle has been worked out during two and one half years by Drs.' Röhm, Goldmann and Stutz, with a large number of experiments on goat, lamb, calf, ox, cow, pig and other skins. At first they generally obtained no white hides, but only scraps from the unhairing vats, in which much bacterial action set in, and it was a long time before they succeeded in finding a means of rendering the unhairing liquids sterile.

Sterilization was first done with mercury salts, then with copper salts, and finally it was discovered that the best means was cresol soap. Pancreatic tryptase is the best, with an alkali, soda, ammonia or borax. In the case of dry hide substance a soak is used before the tryptase containing a little caustic soda, but the caustic soda must be neutralized with bicarbonate of soda, or something similar before the tryptase is added, because the latter is harmed by caustic soda. The action of the tryptase takes place also in neutral or slightly acid solution, but progresses slowly. The quantities of the above materials and the times must be adapted to the hide under consideration. In general however the process lasts four to eight days including soaks. The difference between this process and others is that the unhairing is accomplished, not by lime and the unknown reactions taking place in the lime liquors, or by sulphides; but by the tryptase which formerly was used only for bating, in the form of dog dung, pigeon dung or Oropon. This process also accomplishes the dissolving of interfibrillar substance, the usual action of the bate, at the same time with the unhairing. Thus bacteria lime, sulphides and bates are all together with their harmful effects left out.

The most important result of the absence of bacteria is a larger rendement, which can be seen in upper leather in better feel, and in sole-leather in weight; glue stock gives a greater output for the same reason.

Other results are the avoidance of bad smells, of lime stains, on the leather, of lime sores on the hands of the workers, of harmful waste water for all the materials put in are used up. Finally this chemically controllable process allows an analysis of the hide into its component parts—fiber, refuse, hair or wool—and only the refuse is dissolved while all else is retained. Röhm and Haas, Darmstadt, use this process with great success for glace, goat and sole leather, leaving no doubt that the process is practical for all sorts of skins. This process, free as it is of bacteria puts the whole preparation for tanning hides on a simpler basis. It systematizes and renders controllable the unhairing and bating, and is also much easier to learn. The process has been named Ara-Aescher.

Discussions of the above at the convention of the German section.

Dr. Röhm answered a question by Dr. Gross, by saying that the new process gives a larger amount of hide-substance, than the lime process,

and that hide thus treated can be boiled down to glue much more quickly than limed hide.

Dr. Mayer said that non-poisonous glue stock is the best.

Dr. Röhm explained that the soap used as disinfectant could be easily left out, and further that the phenol and kresol boil away so that by his process one finally obtains a non-poisonous glue.

Dr. Eberle expressed the opinion that a watery extract of the pancreas does not loosen the hair, and that in Dr. Röhm's preparation no pure pancreas tryptase is used, and that the accompanying material is perhaps what has effect.

Dr. Röhm answered a question by Dr. Gross, by saying that the new enzyme was alike whether pure or crude enzyme is used. E. A. B.

Castor Oil. ROGER MARES. *Farmers' and Grape-growers' Review* of North Africa, through *Les Matieres Grasses,* June 25, 1913, p. 3137. England and United States are the principal consumers of this oil. It is used as a lubricant and for greasing harness and shoe leather. It is the base of Turkey red oil. It is used in connection with the making of cotton fabrics. It is used in making soap. The oil-cake cannot be used as cattle-food, as it contains a poisonous substance, ricin. It contains about 1 per cent. of potash, 2 per cent. of phosphoric acid and from 3 to 7 per cent. of nitrogen. as well as from 5 to 18 per cent. of oil. It is an excellent fertilizer, and in India is also used as a fuel and for the manufacture of illuminating gas. A good quality of seed contains 45 per cent. of oil, of which about 32 per cent. is extracted The castor bean plant is a native of the tropics, where it attains a height of 30-40 feet. In temperate climates it grows to a height of 7-10 feet. It is cultivated in India, Java, Brazil, the United States, Africa, Australia. Persia, and on the shores of the Mediterranean. There are many varieties, only a few of which can be grown in temperate climates. In France the seed is planted about April 1, in deep soil, from 4 to 7 feet apart, and at a depth of about 1 inch. Frequent cultivation is beneficial. In warm countries the main stem is cut back to promote the formation of branches and flowers. In Algeria the plants continue to yield for 7 or 8 years, and the crop sometimes reaches a ton of seed per acre. Florida and Texas equal this, but in more northern climates 600 to 1,000 pounds is as good as can be expected. L. B.

Estimation of Free Acid and Basicity of Aluminum Sulphate. W. N. IWANOW. *Chem. Ztg.,* Vol. 37, pp. 805-6; 814. These determinations are difficult and unreliable because of the peculiar behavior of aluminum salts in the presence of water. They freely hydrolyze. $Al_2(SO_4)_3 + 6H_2O \rightleftharpoons Al_2(OH)_6 + 3H_2SO_4$. In such a solution methyl orange and litmus indicate acid. Aluminum hydroxide is practically neutral to phenolphthalein, so that titration of aluminum salts with these indicators results as if only acid were present in the solutions. Various methods have been

suggested: (1) Direct titration with tropæolin, methyl orange, Congo red, ultramarine, logwood etc.; (2) Precipitation of the aluminum with ammonium magnesium phosphate and titration of the free acid in the filtrate; (3) Extraction of the free acid with alcohol. Methods of the first and second kinds have been found unsatisfactory. The method of Beilstein and Grosset is of the third type. It has been widely accepted by writers of text-books. Two grams of substance are dissolved in 5 cc. of water, 5 cc. saturated ammonium sulphate solution added, thoroughly mixed and allowed to stand for some time. Fifty cc. of alcohol are now added, the precipitate filtered off and washed with another 50 cc. of alcohol. The filtrate and wash alcohol are evaporated, the residue dissolved in water and titrated with NaOH and methyl orange. The author conducted a series of experiments, using three kinds of aluminum sulphate commercial, C. P., and basic. The method of B. and G. shows free acid in all of these, and the quantity depends on the amount of water used for solution and the amount of alcohol used in washing.

The author has worked out a new method, based on the fact that neutral salts of aluminum are precipitated in nearly boiling solution by potassium ferrocyanide, while the free acid remains in solution and may be titrated with NaOH. The precipitation must not be carried out at a temperature above 85°C., or hydrocyanic acid will be liberated. After the addition of ferrocyanide, excess of barium chloride is added, precipitating the free sulphuric acid and liberating an equivalent amount of HCl. The excess of barium chloride combines with the ferrocyanide. The presence of iron is no hindrance, as it is thrown down with the other precipitates. Dissolve 1 g. of the substance in 50 cc. of water in a 100 cc. Erlenmeyer flask. Heat to about 85°C. and add 12 cc. of an 8 per cent. solution of potassium ferrocyanide, with constant stirring. Add 20 cc. 10 per cent. barium chloride solution, agitating the contents of the flask vigorously. Transfer the whole to a 100 cc. graduated flask and fill to a point 1/4 cc. above the mark, to compensate for the error due to the volume of the precipitate. Now let the ppt. settle. In half an hour 25 or 50 cc. may be withdrawn for titration, using N/10 NaOH and methyl orange. Results by this method average 1/4 per cent. lower than by that of Beilstein and Grosset. If the clear liquid after the settling of the precipitated material has a yellow color and alkaline reaction, the albumin compound examined is basic. How basic it is may be estimated by titrating the liquid with acid.

L. B.

The Differential Staining of Bacteria in the Investigation of Tuberculosis, and its Application in the Qualitative Examination of Pelt. Dr. Erich O. Sommerhoff, Turin. *Collegium,* 1913, pp. 377-80. A bacterial cell may be considered as an albuminous cell content rich in water, contained in an albuminous membrane of small water content. The cell-wall may be regarded as produced from the albumen-water jelly contained in

the cell, by evaporation. The bacillus of tuberculosis differs from others in being only slightly stained in the cold by methylene blue. It is strongly colored by hot carbol-fuchsin. The customary method is to color the sample of sputum or tissue with hot carbol-fuchsin, then treat with dilute acid for a few seconds, which washes the red color out from the other bacteria, but does not affect the tubercle bacilli. The sample is now stained with methylene blue, which affects only the other organisms and tissues. The tubercle bacilli are thus bright red, the other parts of the sample being blue. It is seen that there are two sorts of colloidal albumins, one which swells in the cold and is easily stained, and another which colors slowly in the cold and only swells when heated. The behavior of the first kind may be studied with egg-albumen, and the second with fresh meat jelly: (artificially prepared gelatin is unsuited on account of the SO_2 used in its preparation). The author designates these two kinds of albumin as alpha and beta, respectively, and regards them as analogous to the colloidal alpha and beta stannic acids. He suggests that membranous tissue of the beta variety, but as it swells, and approaches more and more nearly to solution, the hypothetical ultra-microscopic colloidal particles increase their water content, and so approach the condition of the bacterial cell content, or alpha-albumin. In a colloid albumin solution at ordinary temperatures, both alpha and beta albumin-cells are present, the former being in excess in some cases (egg-albumin), and the latter in others (meat jelly.) The cells which are most swollen permit diffusion of the colloid stain solution through the cell wall, and within the cell the molecule of coloring material unites with the molecule of albumin to form a more complex molecule. This union is accompanied by the splitting off of water, and the colored albumin cell passes into the less active gel condition. When the coloring matter is strongly crystalloid in character, the cell membrane is sometimes ruptured (coagulation). A colloid albumin solution carefully freed from electrolytes, evaporated in a flat-bottomed dish, gives a membrane like an unorganized hide, containing innumerable alpha and beta albumin cells. If the evaporation has been carried out without coagulation, the hide may be swelled with water, and the reactions of the two kinds of albumins again observed. It is apparent from the histology of organized hide that there are laws as yet entirely unknown which govern the behavior of colloid albumin solutions. If a piece of swollen hide be treated with methylene blue, some parts will be more deeply stained than others, these parts being richer in alpha cells. This kind of examination is of interest to the tanner, since his work is done in the cold. Following the analogy of bacteria, whose living and active cells color most easily, fresh hide takes the color better than stale. To the glue-maker, on the other hand, the behavior of the material with carbol fuchsin at higher temperatures is of more importance.

L. B.

The Tannage of Hide By Means of "Insoluble" Metallic Jellies, and their Influence on Tannin Analysis. DR. ERICH O. SOMMERHOFF. *Col-*

legium, 1913, pp.381-2. Freshly precipitated insoluble phosphates, hydroxides, sulphides, and silicates of the heavy metals will tan hide. The tanning action depends on simple mechanical absorption, in contrast to ordinary tannage, which takes place in water solutions, and in which chemical processes play a part. Copper sulphate was precipitated with sodium phosphate in the cold. The fresh precipitate was filtered off, thoroughly washed and then mixed with distilled water. A piece of hide was treated with this mixture in a shake apparatus, and in 2 hours was fully tanned. The leather being dried at 80°C. was found to have an ash content of 13 per cent. the hide before tannage having an ash of 4 per cent. Comparable results were obtained with cold precipitated chromium hydroxide, tin hydroxide, copper sulphide and ultramarine. These results suggested that the tanning effect of vegetable liquors containing insolubles might be partly due to the direct absorption of phlobaphenes ("reds"). Since modern tannin analysis takes account of soluble tannins only, it does not fit the conditions of practice, and often gives results which are too low, since undissolved tannins in colloidal suspension will tan. Dr. Sommerhoff requests that he be permitted to reserve to himself for a time the further prosecution of this interesting research. L. B.

Chemistry of Pickles. G. GRASSER. *Technikum*, 1913, p. 105, through *Collegium*, No. 519. The most used pickle is a solution of salt and sulphuric acid of about 8° Baumé, containing from 8 to 10 per cent. of salt and 1 to 2 per cent. of strong acid. The reactions possible in such a system are discussed, and it is concluded that in the pickle as prepared only salt, sulphuric acid and hydrochloric acid are present

Tanning Hides With Freshly Precipitated Sulphur. DR. CARLO APOSTOLO, Turin. *Collegium*. 1913, pp. 420-1. Leather made by the 2 bath chrome process with the use of sodium thiosulphate as a reducing agent contains free sulphur, sometimes to the extent of 4 per cent. The presence of this sulphur determines to some extent the character of the leather, which is particularly suited for automobile tires and certain other purposes demanding a very tough and flexible leather. It is also known that solutions of sulphur in carbon disulphide have a tanning action. The experiments of Dr. Sommerhoff suggested to the writer the possibility that precipitated sulphur might have a similar action. He accordingly placed a piece of hide in a solution of sodium thiosulphate to which some lactic acid had been added. When the hide had been drummed in this cloudy liquid for a time, it cleared. More lactic acid was then added and the process continued until all the thiosulphate was used up. The piece of hide was found to have been converted into a beautiful white soft leather. If all the acid is added at once, the tannage proceeds in much the same manner, but the resulting leather is much less soft. The sulphur-tanned leather withstands the action of cold water. It does not swell upon lying for 24 hours in cold water, and on being again dried its

properties as leather remain. Carbon disulphide removes but little sulphur, which the author believes to be mechanically combined sulphur. A sulphur determination shows from 2 1/2 to 3 1/2 per cent. The leather does not withstand hot water. L. B.

Action of Salts of Bismuth on Skins. F. Garelli and C. Apostolo, Turin, *Collegium*, 1913, pp. 422-4. It is not possible to obtain clear solutions of salts of bismuth in water, since the salts hydrolyze, precipitating basic salts and liberating acid. If a piece of hide be put into this liquid, it at once swells because of the free acid. The authors, following the directions of Vanino and Hauser (Z. f. anorg. Chem. 28, 210, 1901.) obtained clear aqueous solutions of nitrate of bismuth by intimately mixing 2.5 parts of the salt with 1 part of mannite, and then adding water slowly. The solution may be much diluted and will remain clear for some days. On adding a little of a concentrated solution of salt to the clear solution of bismuth and mannite, a precipitate formed, which redissolved in excess of salt. A solution thus prepared, containing from 1 to 1 1/2 per cent. of bismuth, has remarkable tanning power. A piece of sheep-skin prepared for tannage in the usual manner agitated in this solution fixed an amount of bismuth greater or less depending on the time of treatment. When withdrawn and dried in the air, the hide had a horny appearance, but on being stretched and drawn over a board it resembled white alum leather, very smooth and flexible even without oiling and finishing. On cutting it the fibers were found well separated. Similar but less satisfactory results were obtained without the use of salt in the bath. In this case a white precipitate forms when the hide is put in. The quantity of ash varied from 8 to 18 per cent., the greatest percentage of Bi_2O_3 being about 6. One can hardly say that the hide is tanned, for even in the cold water penetrates it quickly. It swells, and after three hours is practically restored to the condition of white hide. The bismuth is found after this treatment in suspension in the water. L. B.

Tanning With Fatty and Resinous Acids. F. Garelli and C. Apostolo. *Collegium*, 1913, pp. 425-8. The tanning action of oils is due chiefly to the fatty acids, which are easily fixed and firmly retained by the hide. The action of neutral glycerides is entirely mechanical, they lubricate the hide, but do not tan it. Hide is placed in an emulsion made with 3 parts of fatty acid, neutralized with ammonia and diluted to 100 parts with water and shaken for 5 or 6 hours is completely tanned. It is then treated with 1 per cent. lactic acid to break up the ammonia soap and neutralize the excess of ammonia, then dried in the air, stretched and manipulated. The leather produced is white, soft and supple, and resists the action of water, even hot. The results of this experiment do not accord entirely with the theory of Fahrion, who attributes tanning properties only to those unsaturated fatty acids which have more than one double bond. According to Fahrion, oleic acid would not be a tanning material at all. G. and A. find that not only does oleic acid tan, but also palmitic, stearic,

capronic, capritic, etc., under conditions which make it improbable that any oxidation phenomena took place, oxidation being, according to Fahrion, indispensable to oil tannage. The authors have found that in order to fix fatty acids on the hide it is not necessary to have them in alcohol solution, (Knapp), nor to combine them with ammonia and dissolve the soaps in water, (Garelli), for insoluble fatty acids suspended in water tan the hide as well as alcoholic solutions or aqueous solutions of ammoniacal soaps. Ammoniacal soaps in solution hydrolyze, so that a part of the fatty acid is present in colloidal suspension, while a part is in solution, combined with ammonia. It has been usual to attribute the tanning action to the dissolved part alone, but, as has been shown, the suspended part tans also. This accords with the observation of Sommerhoff that colloidal suspensions of insoluble tanning materials will tan. The convenient method of preparing aqueous suspensions of fatty acids is as follows: dissolve 5 parts of stearic acid in a little alcohol and add slowly hot water (about 100 parts), shaking until the liquid cools. If desired, the emulsion may be made simply by shaking, without the use of alcohol. Hide shaken 10 to 12 hours in this cloudy liquid, then dried and manipulated, makes a white, opaque, soft and supple leather, with all the characteristics of oil-tanned skin. Kept 24 hours in water it does not swell and on drying and working it, it is found opaque and supple as before. It is therefore leather according to the definition of Knapp, modified by Fahrion. Its water resistance is small, determined by Fahrion's method about 30, somewhat higher than that of alum leather. Ether does not dissolve out all of the fatty acid. After ten extractions with ether in a Soxhlet, it remains leather. Boiling alcohol removes only a part of the fatty acids, the portion which was mechanically held. By titrating the alcoholic solution, the proportion of the fatty acid which was uncombined may be determined. Titration of 3 samples gave an average of 7 per cent. of fatty acid (as stearic) removed by alcohol. In order to remove the portion of fatty acid which is left after treatment with alcohol or ether, it is necessary to use hot caustic alkali. The amount removed thus from the same three samples mentioned above averaged 2.3 per cent. The unsaturated fatty acids with more than one double bond probably tan much more energetically than the saturated acids, and make a leather with higher resistance, but it seems certain that the saturated acids have a true tanning action. Rosin behaves like the fatty acids, but the leather formed is less soft than that made by fatty acids. L. B.

Chrome Leather from Dry Hides. *S. & L. Rep.*, July 31, 1913. Dry hides which after soaking do not show defective grain may be made into good chrome leather. Some sodium sulphide should be used in the soaks. The writer recommends unhairing with sulphide, using a clear solution, made up to a liquor of about 7° bk. The hides should be taken out at the end of each 24 hours and the liquor plunged. The time re-

quired is about 3 days. After unhairing, the hides are soaked for 3 days in a weak lime. They are then split, bated with a bran bate, to which a pint of lactic acid has been added for each 100 pounds of hide. They are then pickled in a solution of 12 pounds salt and 1 1/2 pounds formic acid to 100 gallons of water. The one-bath process is used, 6 pounds of dry material being needed for 100 pounds of grains. Dissolve in 2 gallons of boiling water. The pickled grains are drummed with 8 gallons of water and 6 pounds salt for 15 minutes. Then 1/3 of the chrome liquor is run in and the drum run 1/2 hour. A second portion is added and the drum run another 1/2 hour. The last third being added, the drum is run 1 hour, after which 1/2 pound of bicarbonate of soda in a little water is put in. The drum is now run 2 hours, 6 ounces more bicarbonate added, and the drumming continued until the tannage is complete, the test being to boil a piece and see that it does not curl. After draining 48 hours, neutralize in the drum 1/2 hour, using 1 pound of borax for each 100 pounds of leather. Wash for 1/2 hour. The leather is now ready to be shaved, colored and fat-liquored.

A Color Reaction of Gallic Acid and Tannin. O. SCHEWKET. *Biochem Zeitsch.* 1913, vol. 52, pp. 271-4. Through *J. S. C. I.*, July 31. If 3 cc. of a solution of iodine in potassium iodide be shaken with 2 cc. of a 1 per cent. solution of gallic or tannic acid, and then 300-500 cc. of tap water or of a very dilute solution of alkaline carbonate or other alkaline salt (borax, sodium phosphate, etc.) be added, a reddish violet coloration is produced. The coloration is prevented by even dilute mineral acids, but is not prevented by dilute organic acids. Caustic alkalies and alkali carbonates in high concentrations give a dirty brown color, but the alkali salts of organic and weak inorganic acids (boric and phosphoric) produce the red-violet color even in relatively high concentrations The iodine must be in excess, as excess of tannin itself prevents the reaction. By this test gallotannic acid may be distinguished from other tannins, (kino, catechu, cinchona tannins, etc.) so far as these are free from gallic acid. The reaction may also be used for detecting gallic acid or tannin in plants and pharmaceutical preparations, for testing a solution in regard to alkalinity, and for distinguishing organic from mineral acids.

Natal Wattle Bark for the United States. CONSUL N. B. STEWART, Durban, South Africa. *Consular and Trade Reports.* In order to try to develop a market in the United States for Natal wattle bark, an association composed of the principal wattle growers in the Province has just completed arrangements for forwarding 500 tons to certain American tanners for experimental purposes. The bark is to be shipped as soon as a vessel is available for direct transportation, which will be during June or July. There will probably be a loss to the exporters on the shipment. If such is the case each producer in the association will

eventually pay a part of it in proportion to his output of bark as a contribution toward the development of a new market.

At present the wattle bark output of Natal goes chiefly to Hamburg, which fixes the price of the product. The producers believe that there is an agreement among the Hamburg buyers which tends to lower the price, and it is for this reason that they are most anxious to find another market which will compete with the German.

The price of wattle bark has declined very much within the past two years. The average in Durban, f. o. b., January 1, 1912, was about £5 10s. ($26.77) per ton of 2,240 pounds, compared with a little under £5 ($24.33) per ton on January 1, 1913. Since January the price has further declined, and producers are somewhat depressed over the outlook for the future of the industry. They say it is doubtful if it will expand so long as prices are below £5 10s.

The total output of bark in the Province in 1912 was about 52,000 tons. It is estimated that it will reach 70,000 tons during 1913. During the next five years, with the area now planted, the output should reach 100,000 tons per annum. If present prices continue, however, there will almost surely be a decline in production after the growing trees have matured.

As no shipments of wattle bark have yet been made to the United States freight rates on it can not be quoted. The freight per ton of 2,240 pounds from the wharf Durban to wharf London or Hamburg is £1 7s. 3d. ($6.63). The actual freight is £1 5s. ($6.08), and wharf charges are 2s. 3d. ($0.55) per ton

Viscosimetry. W. F. Higgins. *J. Soc. Chem. Ind.* Vol. 32, pp. 568-73. June 16, 1913. The experimental work described in this paper is in effect a comparison of the Engler and Redwood viscosimeters with an instrument measuring absolute viscosity. The absolute viscosimeter employed is of the type of the Ostwald instrument, described in the January, 1913, Journal, p. 49. The capillary is horizontal, connected to the vertical reservoirs by rubber stoppers, so that a capillaries of different sizes may be used for oils of different viscosities. The apparatus is so arranged that additional air pressure may be exerted on the oil during flow, in the case of oils whose viscosity is high. Methods of calibrating the capillaries are described. Curves are given showing the change of viscosity of oils with temperature. Tables are given for converting readings on the Engler and Redwood instruments into absolute viscosities.

Notes on the Theory of Fat-liquoring. J. B. Salomon. *Tanners' Year Book,* 1913, 143-5. A fat liquor is essentially an emulsion of an oil, generally mixed with a soap. Chrome leather will completely absorb this mixture, and is thereby softened. It is supposed that the soap is hydrolyzed into its alkali and fatty acid constituents, and that the acids enter into combination with the basic chrome salts on the tanned fibers producing a chrome soap, insoluble in water, which fills the interfibrillar

spaces, producing a waterproof and pliable product This theory is weakened by the fact that a hard soap makes a more or less caky leather, while a soft soap does not. If the alkaline soap were decomposed and a chrome soap formed, the effect should be the same whichever kind of soap was used in the fat-liquoring process. It would seem, therefore, that the soap itself is taken up, at least to some extent Another objection to the chrome soap theory is the fact that soap fat-liquors are taken up by vegetable tanned leathers. The oil is the more important part of the fat-liquor. It is assumed that the minute oil particles of the emulsion penetrate the leather and are deposited on the fibers, thus acting as a simple lubricant. This is probably partly correct, but not entirely satisfactory. It does not account for the difference between fat-liquored leather and that which has been simply oiled, even with a larger amount of oil than was used in the fat-liquor. The oiled leather is not so supple as the other. Degreased chrome leather is much softer than that which has never been fat-liquored. This seems to show that some, at least, of the oil is chemically fixed by the fiber.

The Acidity of Vegetable Tannins and Vanicek's Method of Tannin Analysis. R. LAUFMANN, Freiberg Versuchsanstalt. *Collegium*, 1913. pp. 382-8. Vanicek's proposed method of estimating tannin was published in *Zeit. Angew. Chemie*, XXVI, pp. 68-70, (Abstr. this J. March, 1913, p. 150.) He proposes to establish an acid value for each variety of tannin. To determine the amount of tannin in any liquor two titrations would then be necessary, one of the original liquor and one of the residue after detannization. The difference multiplied by the factor for the kind of tannin known to be present gives the tannin content. Laufmann has determined the "tannin acid number" of several important tannins. He finds those of the pyrogallol tans to range between 211 and 271 (mg. KOH per g. tannin). For the protocatechin tannins the range is from 81 to 133. Values in the case of individual tannins vary by amounts ranging from 1 1/2 to 22 per cent. of the entire value. He observes that since tannins have but a small acidity and one liable to great variation in the case of the same tannin, unavoidable errors of titration would introduce relatively great errors in the results. He inclines to the view that the tannins consist of an acid substance united to a quantity of neutral material, larger in the case of the protocatechin tannins and smaller in the case of the pyrogallol tannins. L. B.

Hints for the Manufacture of Leather Belting. W. EITNER. *Gerber*, 1913 [39], 71-3, 85-8. Vegetable or chrome tannage as well as combinations are used according to the product desired and the nature of the available hide, heavier hides being suited for chrome. Where both methods are used it is of advantage to employ the same liming process, permitting a sorting of the white hide; the liming used for sole leather is suited. The salted hides are soaked in fresh water for 12 hours which is then changed. The watering need not be pushed since a little salt

retained is not unfavorable and loss of hide is avoided; hard spots may be softened on the beam. To secure high yield and lessen stretching of the leather, sodium sulphide alone, 1½ per cent., is chosen for unhairing. After this to produce a soft grain an after liming would be too vigorous. Nor are acid baths desirable since de-liming is not required and a brittle grain may result with vegetable tannage. A short light bate with fowl dung or Oropon E will give the desired effect. A few hours watering is sufficient when there is no lime in the hide; this minimizes loss of hide, particularly for chrome leather.

With vegetable tannage it is not easy to obtain good yield and quality without loading the leather with tannin which is undesirable in belting. Hence but a moderate use is made of the drum and sufficient time should be given to the fore and after-tannages. For the vats, 10 suspenders are used, the hides remaining one day in the first, 3 days each in the others. The liquors for this lengthy fore-tannage are derived from the used lay-aways and are strongly acid producing a marked swelling. After the fore-tannage, 2-3 lay-aways (Versenke) are used, with liquors of 25, 28 and 32 degrees barkometer. For dusting, oak bark, or 70+30 pine and quebracho are taken. The time is 12, 15 and 20 days. When extracts are used, chestnut wood or cold solution non-sulphited quebracho are suited but not Argentine extract. Following the "Versenke" the tannage is finished in a lay-away (Satz) of 4 weeks in order to give weight without lowering quality. Rapid work in the drum would merely impregnate with tannin mechanically and unevenly and most of this would be removed by the thorough washing necessary before greasing. If similarly drum tannage were substituted for the 4 weeks tanning in the "Versenke," an inferior product would result which could be improved by leaving 4 weeks in a lay-away, dusting with pine, oak or willow (mixed with quebracho if desired) and steeping with a used drum liquor diluted to 25 degrees.

The aim in currying is to remove as little tannin as possible and to introduce the maximum of fat, operations which do not harmonize together. The washing is often effected with the brush on the table which hardly suffices; 24 hours leaching in water removes unfavorable extractive substances. To avoid loss, the tannin may be fixed with glue according to the process lately described by the author and favorably reported on by correspondents. As for washing after the hot greasing, the chief effect is to remove materials used in dressing and their employment vain. Cold greasing formerly employed gave at the most 12 per cent. increased weight or half the present requirement. Hot greasing, the so-called "burning in" is increasing in practice; this at temperatures of 145°-212° F. permits large quantities of hard fats to be taken up. By heating with steam, 100° C. can be used. Much leather of to-day will not withstand this heat; it should be perfectly dry, neither does drum tanned leather bear the heat well. Mineral fats (paraffin) are much used in mixtures; the belting does not cement well when they are present and

rosin is added to counteract this. To bleach highly greased croupons, they are kept a few minutes at 35° C. in a 3 per cent. bath of NaOH, then rinsed in lukewarm water and bleached in a cold bath containing 5 per cent. white hydrochloric acid.

For chrome leather belting, very heavy hides are preferred. After sorting the white hides those selected for chrome tannage are cropped and the offal reserved for vegetable tannage. When the greenish color of chrome leather is not desired, a light vegetable tannage is first given or the hides are brushed with gambier and glycerin. Chrome leather belting has high breaking resistance but stretches, especially double bath leather, hence the single bath process only is available. To secure a uniform and gradual tannage vats are used. Under-tanned leather stretches, over-tanned tears; the intermediate stage is attained by using weak liquors and considerable time. Eight vats are used, 2 days to each. For example, chrome alum is used in the first 3, finishing at 20 degrees barkometer. The remaining 5 are basic finishing at 35 degrees, the liquors containing 100 parts chrome alum in 300 hot water, with addition of 10 parts calcined soda. After tannage, the leather is watered twice. Before nailing to dry it is treated with 1 per cent. neutral oleate fat, ½ per cent. vaseline oil, or the grain is oiled with heavy mineral oil. The hot process is always used for greasing to insure good rendement.

W. J. K.

Fish Leather. W. Eitner. *Gerber,* 1913 [39], 183-5, 197-9. The skin of fishes resembles that of reptiles in structure, except that the outer skin of reptiles, generally horny scales, is represented in fishes by a mucous coat. The scales of fishes are really part of the leather hide. This, like that of reptiles, consists of parallel fibers crossing each other like woven textiles, differing from the felted structure of the hide of mammals. The leather is therefore very strong, but not elastic or soft, although it may be prepared to bend easily. Fish skin does not resist alkali or alkaline sulphides, is sensitive to acids and easily putrefies. Dried skin is more resistant but putrefaction begins before it can be fully softened in pure water.

Some 25 years ago skins from a sort of ray in the East were in the market. Their value lay in a peculiar pearly armor firmly fixed to the skin, constituting its grain. Their use was chiefly for ornamental leather, book bindings, hand bags, etc. The skins were softened with 5 per cent. calcined soda (hide = 100), sodium sulphide giving spots. The flesh was carefully removed and the grain scrubbed. A pure lime was then used for 8-12 days serving to loosen the hide fiber. After watering and sorting, the white specimens were bleached with chloride of lime. The rest were generally dyed and before tanning. The tannage was light and not an important operation since the valuable part of the leather, the pearly armor, was incapable of being tanned. Later this pearl fish leather was used for ladies' belts, etc., and was then tanned with formaldehyde.

After bleaching, the skins were treated in the drum with 2 per cent. soda, 4 formaldehyde, 1 bone oil, 100 water at 20°R for 3-4 hours.

Another class of fish has the skin covered with scales, of which a Japanese carp or parrot fish is an example. The softening of the dried skin only proceeds from the flesh side and the water must be continually removed or else "sharpened" with soda; sulphide can be used if the scales are not to be preserved. After removing the flesh the scales are brushed if to be retained, otherwise removed before liming. The liming (pure lime) lasts 8 days with scales, 4 days without. De-scaled skins are delimed cautiously with acid and then receive a light fowl dung bate. Acid is not used for hides with scales and they go directly into a bran bate at 20°R. The tannage is simple, with oak, Japonica, sumac or cold soluble unsulphited quebracho.

A third class of fish yielding skins available for tanning are those having naked skins like the ell-pout or burbot. The fresh skin is treated with pure lime for 6 days in winter, 4 in summer. After washing, it is well to salt the skin and let it lie 2 days to prevent shrinkage of the hard grain during tanning. Light tan stuffs are used in weak liquors.

A fourth type is that of the sharks in great variety. In all these the grain is covered with fine prickles. The skins from Mediterranean sharks (Katzenhaie) come dry and are softened in a 2 per cent. sodium sulphide bath for 2-3 days. The flesh is removed, the grain scrubbed and the skins are then placed in a lime sharpened with sodium sulphide for 8-10 days. After washing and shaving, a bate is given of 6.6 per cent. salt, 1.3 hydrochloric acid (white hide = 100). Sumac, Japonica or some light tan is used; the tannage proceeds slowly. Formerly this leather was only used for abrasive purposes and did not even require tanning. Now an important operation is the grinding off the sharp silicious prickles of the grain on a carborundum wheel. The polished bony stumps of the spines give a peculiar ornamental effect to the leather and can be dyed. The large salted shark skins from the extreme north are simply watered, then limed 12 hours and worked further as above. The outer layer with its prickly growth can be split off by machinery leaving a fine felted strong material suited for any use of buffed leather.

W. J. K.

PATENTS.

Tanning Agent. British Patent No. 8,512. J. Y. JOHNSON, 47 Lincoln's Inn Fields, London. Badische Anilin und Soda Fabrik. A soluble aromatic compound obtained from formaldehyde, or a body giving rise to formaldehyde and an aromatic phenol or phenol derivative, the compound containing one or more acid salt-forming groups, beside a hydroxyl group. If the condensation products obtained be insoluble or soluble with difficulty, they must be treated with sulphonating agents. Fifty-

four parts of formaldehyde, (30 per cent. by vol.) are treated with 174 parts of paraphenol-sulpho acid at a temperature not exceeding 35° C. The solution is then nearly neutralized by an alkali, and when diluted to 0.5° Baumé is used as a tanning bath, and gradually strengthened to 5° during 10 days.

Impermeable Leather. British Patent No. 8,603. W. R. SMITH and J. D. LARKIN, Buffalo, N. Y. Cut soles are drummed in a hot mixture of bituminous substances.

Impermeable Leather. British Patent No. 8,974. T. H. RAMSDEN, Bramhope. Tanned sole leather is rendered durable and impervious by being passed between rollers which apply boiled linseed oil to the flesh side and force it in by pressure.

Leather Staking Machine. U. S. Patent No. 1,070,731. E. J. Quirin, Tioga Center, N. Y.

CORRECTION.

In the August number, p. 318, ninth line from bottom, instead "best described under (9)," read "best described under (10)."

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LLOYD BALDERSTON . . . . Associate Editor

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ELECTIONS.

ACTIVE.

Roy J. Bailey, Elkland, Tioga Co., Pa.

James A. S. Morrison, M. Sc., % Clark, Son & Morland, Ltd., Glastonbury, Somerset, England.

COUNCIL MEETING.

The Council met in New York on Sept. 6th. The members were all present except Messrs. Reed and Hoppenstedt. The Secretary's report showed the total membership on Sept. 6th. to be 135 active and 144 associate, total 279.

It was decided to hold the annual meeting in Atlantic City, N. J., on December 4, 5 and 6.

To serve as a committee on program, Messrs. Reed, (chairman), Griffith, Wallin, Teas and Alsop were chosen, with liberty to add to their own number if they choose.

TENTH ANNUAL MEETING.

The tenth annual meeting of the American Leather Chemists Association will be held at the Hotel Traymore, Atlantic City, N. J., on Thursday, Friday and Saturday, Dec. 4, 5 and 6, 1913.

NOTE ON ANALYSIS OF MOELLON.

NEWARK, N. J., August 25, 1913.

EDITOR JOURNAL AMERICAN LEATHER CHEMISTS' ASSOCIATION,

DEAR SIR:—

I have noted with considerable interest the analyses of some samples of wool grease by Mr. Chas. Eachus. It would appear from this that the unsaponifiables in ordinary wool greases run in No. 1 25.03 per cent., moisture 0.37 per cent., to No. 5, unsaponifiables 33.52 per cent., moisture 0.94 per cent.

My interest is called to this because of a recent analysis of a moellon which I have made which occasioned some criticism. I have found on 32 samples of cod oils known to be pure that the moisture at no time exceeded ½ of 1 per cent., and that the unsaponifiables were 0.90 per cent. (average).

On 12 samples of known pure fish oils, the moisture was below ½ of 1 per cent., and the unsaponifiables were 0.84 per cent.

I have found, in looking up my records, that 22 samples of known pure moellons showed 19.43 per cent. moisture and 0.72 per cent. unsaponifiables, which when calculated to a dry basis is equivalent to 0.90 per cent. of unsaponifiables.

From this data it would appear that cod oils show 0.90 of 1 per cent. unsaponifiables on virtually a dry basis; fish oils 0.84 of 1 per cent., and moellons 0.90 of 1 per cent.; at least, such has been my experience.

According to Mr. Eachus, the unsaponifiables in No. 1 and

No. 5, the minimum and the maximum, are 25.03 per cent. and 33.52 per cent., using petroleum ether for extracting purposes.

I have been severely criticised for having reported a moellon which contained 29.50 per cent. moisture and 2.92 per cent. unsaponifiables (equivalent to 4.17 per cent. absolutely dry,) the average of three analyses, as containing wool grease. The unsaponifiables were by test found not to be mineral oils.

This particular moellon was reported as containing from 8 per cent. to 12 per cent. wool grease, by the writer. According to Mr. Eachus' results as published, this would be comparatively low ($4.17 - 0.9 = 3.27$ plus 20 per cent. moisture $= 2.60$ per cent. unsaponifiables above average of known percentage in pure moellons). This would indicate under No. 1, nearly 10 per cent., and under No. 5, 8 per cent. of wool grease adulteration to this moellon, provided the excess of unsaponifiables found was caused by such sort of adulteration.

The questions that I desire to bring before the association are:

First, Is the chemist's analysis of a moellon, other than moisture, of value?

Second, Is not the chemist justified in expressing an opinion when the character of the unsaponifiables and their quantity is such as exists in this case?

Third, Does not the above analysis justify the opinion of the chemist in stating that, in his opinion, a moellon under these conditions contains wool grease?

Fourth, Is it necessary to modify such an expression of opinion to homologues of wool grease, when the absence of mineral oils is established?

Yours very truly,

JNO. H. YOCUM.

VALUATION AND FIXATION OF TANNING EFFLUENTS.

By J. W. Phelan and J. H. Cohen.

INTRODUCTION

The maintenance of better sanitary conditions and the recovery of valuable ingredients are the two important factors in tannery waste purification. Although it has been claimed for a long time that about one half the weight of hide and chemicals used in leather manufacture goes into the effluent, practically no attempt has been made to avoid the loss. The soaks, limes, and tanning liquors are principally responsible for the loss. Although all of this material is rich in nitrogen, the only part recovered is the (sludge) residue left when the waste liquors are allowed to settle or the precipitate formed on addition of precipitants to these liquors; the large amount of nitrogen in the effluent is lost.

Tannery effluents consist mainly of spent tanning liquors, old limes, washings from the soaking, drenching, and tanning processes, albuminoid leather dressings, and dye liquors. These effluents are not clear, and they are sometimes acid and at other times alkaline. If no attempt is made to purify these liquors, the following conditions will inevitably result. Lime liquors and tan liquors will unite to form a brown insoluble compound which may eventually clog the pipes through which they discharge. Any acid liquors present will react on some of the solid or soluble matter and obnoxious gases will be evolved. The solid suspended matter will deposit on the banks of the stream which receives it, thus forming a slime which will render the river obnoxious from both the aesthetic and sanitary point of view. Therefore tannery effluents must be treated so that they cannot have a deleterious effect on the streams into which they flow and upon the public.

The extent to which purification is demanded from the tanner is dependent on the stream into which the effluent is to deliver. As the oxygen absorbed from the air oxidizes much of the organic matter in solution, the ability of a river to purify itself depends upon the opportunity which it has of dissolving this oxygen. A stream which in its course has ready access of air on account of rapids, falls, or whirlpools may recover itself readily while a slow, quiet stream, receiving relatively a smaller amount of

effluent may remain polluted. As there are no means of giving to all streams the same capacity for self purification, it becomes necessary to remove all constituents, from the effluent, which may affect the purity of the river.

The object of the methods of disposal heretofore employed by the leather manufacturer has been principally to purify the effluent in order to comply with sanitary requirements, while he has given but little attention to the large loss of nitrogen taking place.

The methods for the disposal of tannery waste may be divided into two classes, natural and artificial. Natural purification consists of dilution, irrigation, or filtration. In dilution, the waste is discharged into a swiftly flowing stream. As the flow of the stream is so rapid, the insoluble matter cannot settle and fish, water plants, bacteria, and dissolved oxygen render the waste inoffensive. In irrigation, land, on which hardy cereals grow, is watered, as frequently as possible, with the waste. The latter is drained off, partly purified by the action of non-aerobic bacteria in the soil, to the nearest stream. In filtration, the effluent is partly purified by adhesion to the filtering medium, usually sand beds, or by the action of non-aerobic bacteria.

Artificial purification consists of chemical processes as precipitation and forced oxidation in conjunction with suitable filters.

In practically all of the precipitation methods, lime and tan liquors are delivered from separate drains into a tank where precipitation takes place. By this means, the greater part of the tanning matter combines with the lime forming a brown insoluble compound, in which some of the dye and other organic matter becomes entangled, and in this way are removed from the liquor. To aid precipitation aluminium sulphate and iron salts are used. Aluminium sulphate aids principally by forming a colloidal precipitate which carries other substances with it, and iron salts are used to remove arsenic compounds, which if not removed will hinder the subsequent action of the filters.

Only in very rare cases may the clear liquor, obtained after the sludge settles, enter the streams safely. To further purify the liquor various methods are employed. Contact beds, where the liquor remains in beds filled with small broken stone for a short time and is then let out with a brief intermittent resting period

for the bed; sprinkling filters, where the sewage is sprayed on the surface of a deep bed of coarse material through which it passes; septic tanks, where the sewage is retained in the filters long enough to insure its partial purification from organic matter and organisms by the bacteria contained in the filter; sterilization of the liquor with hypochlorites, and forcing ozone-saturated air through the filter beds are methods which are used in connection with the precipitation process. To purify the effluent most efficiently, the liquor from the above outlined methods may be run into settling tanks to remove more suspended matter, and from these through a sand filter to the stream without any danger of pollution.

No attempt was made to recover the valuable nitrogenous compounds, other than to give the sludge to farmers to be used as a fertilizer in conjunction with stable manure. Recently however, the U. S. Department of Agriculture has directed considerable attention to this part of the problem, and has given an estimate of the cost of separating the sludge with a centrifugal machine and drying it for fertilizer purposes. The market value of the product thus obtained is also estimated.

In this investigation, the nitrogen content of tanning effluents will be determined. Methods for treating the effluent to fix the nitrogen will be described. The formation of a compound which may be thrown out of solution and subsequent evaporation of its water content will probably be the desired method. The value of any such compound for fertilizer purposes will be determined. By this means, it is hoped to partly eliminate the present difficulties between the leather manufacturer and the public.

ANALYSIS OF SAMPLES

To carry on this investigation, samples of practically all kinds of tannery waste were analyzed for their nitrogen content by the Kjeldahl method for total nitrogen. The results of these experiments are tabulated in Table 1.

CONCLUSION FROM ANALYSIS

As is evident from the above data, the amount of nitrogen in the liquid waste of a tannery ranges from about one hundredth to several hundredths of one per cent. It is true that in one case

(E) there is more than one tenth of one per cent., but the use of this kind of liquor is comparatively rare, and where it is used it is thrown away in minimum amounts. The results also show what one might anticipate, that the more active the reagent in which the skins were placed the greater would be the loss of hide substance.

TABLE I.

Sample	Type	Parts NH_3 per 100,000	per cent. by wt. of NH_3
A	Tail liquor	27.5	0.0275
B	Tail liquor	25.0	0.025
C	Soak water	9.0	0.009
D	Lime liquor	45.2	0.0452
E	Lime sulphide	133.6	0.1336
F	Comb. effluent to sewer after passing through settling tanks	9.59	0.0096
G	Dried sludge from settling tanks		3.7
H	Combined waste from tan yard and leather finishing departments		
H_S	Dried sludge from H		3.16
H_L	Liquor from H	8.02	0.008
J	Settled lime liquor	7.1	0.007
K	"Puer" liquor	6.8	0.068
L	Dried residue from system employing aluminium sulphate and settling tanks		2.03

The small values of nitrogen content as shown in Table I led to questioning the accuracy of the statement issuing from the Gloversville sewage authorities that fifty per cent. of the weight of hide substance was lost in the tanning process. Average values of the nitrogen content of leather are from eight to ten per cent. From the above statement, one would conclude that an equivalent amount would be found in the effluent. However, calculations made by the use of data from different sources showed that the above statement concerning the fifty per cent. loss is erroneous. Instead of this large loss, there is only a four to five per cent. loss. One may say that the Gloversville sewage people based their calculations on the dry sample and the percentage loss would be greater. This is true but even this would not account for the difference between fifty and four to five per cent.

FUTILITY OF EVAPORATION

The enormous volume of effluent and the cost of evaporation make it evident that evaporation is futile, although by this means the entire problem of sewage disposal and purification would be eliminated. It is therefore necessary to look to other methods to overcome the difficulty.

PRECIPITATION METHODS

Careful consideration of all the methods available in sewage purification led to the conclusion that the best means to recover the nitrogen in the effluent is by chemical precipitation. By this means, a greater part of the nitrogen can be recovered at a minimum cost. The chemicals to be used in this method are lime, aluminium sulphate, and iron sulphate or copperas, and advantage is to be taken of the precipitate which forms when lime liquors are mixed with tan liquors.

The reactions which take place by the use of the above are as follows; the lime neutralizes any carbonates or free acid which may be present in the effluent and renders it alkaline. If carbonates are present, calcium carbonate is formed. It is evident that to an alkaline effluent, as most tannery effluents are, no lime need be added. When aluminium sulfate or copperas is added to the effluent containing free alkali, both of the salts decompose and an insoluble precipitate of aluminium hydroxide or iron hydroxide is formed in conjunction with calcium sulphate. As all of these precipitates are flocculent, they carry down with them by occlusion or by the formation of colloids, soluble organic compounds among which are the nitrogen compounds.

EXPERIMENTS WITH PRECIPITANTS

To verify the previous statements, the following experiments were carried out:

When equal quantities of samples A and E were mixed, a brown precipitate formed and the brown solution remaining was analyzed for total nitrogen by the Kjeldahl method. As a result of this experiment, it was found that by precipitating these liquors, thirty per cent. of the total nitrogen was removed from the effluent.

Various samples, after being made alkaline by the addition of lime, were then treated with copperas. In each case, a flocculent

precipitate was formed and a clear solution was left after the precipitate settled, except in the case of sample A in which case a blue ink was formed due to the union of the iron salt with the tannin compound in the sample.

The results of these experiments are tabulated below.

TABLE. II.—COPPERAS ADDED IN ALKALINE SOLUTION.

Sample	per cent. N as NH_3 removed	Gms. NH_3 remaining in sol'n. per 100 cc.
A	31.4	0.0189
E	44.0	0.0749
F	56.0	0.0042

The same samples were then treated with aluminium sulphate after they were made alkaline by lime. In every case, clear solutions resulted after the precipitate settled.

The results from these experiments are tabulated below:

TABLE. III.—ALUMINIUM SULPHATE IN ALKALINE SOLUTION.

Sample	per cent. N as NH_3 removed	Gms. NH_3 remaining in sol'n. per 100 cc.
A	52.3	0.0131
E	56.7	0.0578
F	66.0	0.0033

From Tables II and III, it is evident that aluminium sulphate is the better precipitant. Primarily, aluminium sulphate does not color the effluent; secondly, it forms a heavier and bulkier precipitate with consequent greater occluding power; and thirdly, soluble salts are not formed with organic acids which are decomposed and clog up filters as in the case of iron.

The above results show that nearly sixty per cent. of the nitrogen which at present goes to waste can be recovered. The commercial value of the recovered sludge, as a fertilizer, depends on the extent to which the nitrogen is available.

With this end in view, available nitrogen determinations were made on some of the samples. The method of analysis is given in Bulletin 107 (Revised) of the U. S. Dept. of Agriculture.

The results are tabulated below:

TABLE. IV.—AVAILABLE NITROGEN DETERMINATIONS.

Sample	per cent. N available
G	54.0
Hs	51.0
$Al_2(SO_4)_3$ ppt. from E	36.7
Copperas ppt. from F	40.1
L	48.5

The general practice of fertilizer makers is to consider the nitrogen as all available when fifty to sixty per cent. of the nitrogen is available.

PRODUCT AND METHODS TO OBTAIN IT

The method to be employed in the recovery of the sludge depends on the space available for said purpose. Where much space is available, a simple settling tank system with periodic removal of the sludge would suffice. Where land values are high and in thickly populated districts some form of rapid separating device as centrifuging or filter pressing should be employed.

The sludge obtained by either method will contain from sixty to eighty per cent. of moisture and this may be dried by the waste heat from other parts of the factory or by the use of a rotary kiln.

Although the effluent from the sludge is quite pure and could in most cases safely enter the streams, if it is desired or necessary to further purify the clear liquor, any of the methods outlined in the introduction will satisfactorily serve the purpose.

The value of the material obtained in this process depends upon its content of potassium, phosphorus and nitrogen, and absence of poisonous matter. The amounts in which the first two ingredients are present in this substance are negligible, but lime is present in varying amounts ranging from two to twenty per cent. As it can be used on acid soils, the presence of lime in the material may increase its commercial value. The presence of arsenic or sulphur may make an otherwise good material worthless for fertilizing purposes, and although sodium sulphide and realgar, arsenic sulphide, are sometimes used in leather manufacture, the presence of these ingredients is very small or negligible. The nitrogen is the valuable ingredient for fertilizer, and although it may only be two to three per cent. of the entire material, it may be used for a filler or body for richer fertilizing material. The commercial value of the dry material will be about six dollars per ton.

SETTLING TANK SYSTEM

When space is ample, land values low, and the country thinly populated, a settling tank system can be efficiently employed to obtain the sludge.

The ground plan of a precipitation plant treating one million gallons of effluent per day is shown in Fig. 1. If the sewage is not alkaline, it must be made so by the addition of lime before aluminium sulphate is added. When required, the milk of lime should be added above the mixing channel. The waste then passes through the mixing channel of baffle plates or step device, while aluminium sulphate is added to the turbid mixture. The rate of flow of the aluminium sulphate will depend on the flow of the effluent. If there is a constant, steady flow, a constant feed of aluminium sulphate can be regulated. However, where

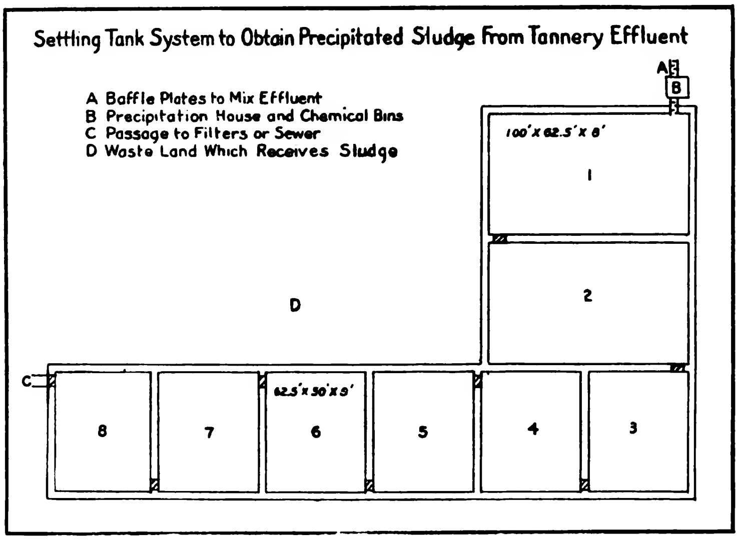

Fig. 1.

the flow is intermittent, an automatic valve arrangement can be employed. After the mixing channels, the sewage flows into concrete tanks 1 and 2 which serve as roughing tanks in which most of the sludge is retained. The partially settled sewerage then passes through the tanks 3, 4, 5, 6, 7, and 8 in series from which it will emerge as a tolerably clear liquid to go to the sewer or for further treatment. The flow through the tanks, averaging ten hours can be controlled by weirs across the outlets of the tanks, and floating substances are prevented from passing off by the use of scum boards.

The sludge amounting to about fifteen cubic yards per million gallons which contains eighty-five to ninety per cent. water collects in the bottom of the tanks from where it can be removed monthly. To remove the sludge, the water is drawn off and the sludge flows down the inclined bed of the tank by a channel to waste land. A large part of the water content of the sludge will be removed by exposing the sludge to the weather while it is waiting for a demand. A demand for the dried material can easily be complied with by drying the material by waste heat. However, a more elaborate plan would be to receive the sludge from the tanks into a sump tank, allow the sludge to settle, drain off the water, and then filter press the sludge which operation can be followed by drying the cakes and these can be used for fertilizer. Although the latter method will give a constant supply of the sludge cake, there will be an increased cost due to more tanks, filter presses, and power.

Although the initial cost of these tanks will be great the depreciation will be small. The cost of treating the effluent will be five dollars for one ton of aluminium sulphate to be used per million gallons, and the cost of drying the sludge will be about one dollar per ton of dried material. Labor will average three and one half dollars per day. The effluent will give about two tons of dried material per day, the value of which will vary from six to seven dollars per ton. Thus, although the profit is not very large and the initial expense is great, it will in many instances be advisable to adopt this method, as it eliminates a great nuisance.

RAPID FILTER SYSTEM

Where land values are high and where the neighborhood is thickly populated, it is evident that for waste purification a rapid system utilizing but little space must be employed. For this purpose, a rapid filtering device recently put on the market, the Moore Slimes Filter, can be utilized.

The principal part of this filter is the filter leaf. Fig. 2 is an illustration of one of these leaves which consists of a rectangular frame of tubing enclosed by sheets of canvas filter cloth and suspended from a rigid bar or header. The side tubes have no perforations whereas the bottom pipe is perforated. The filter cloths

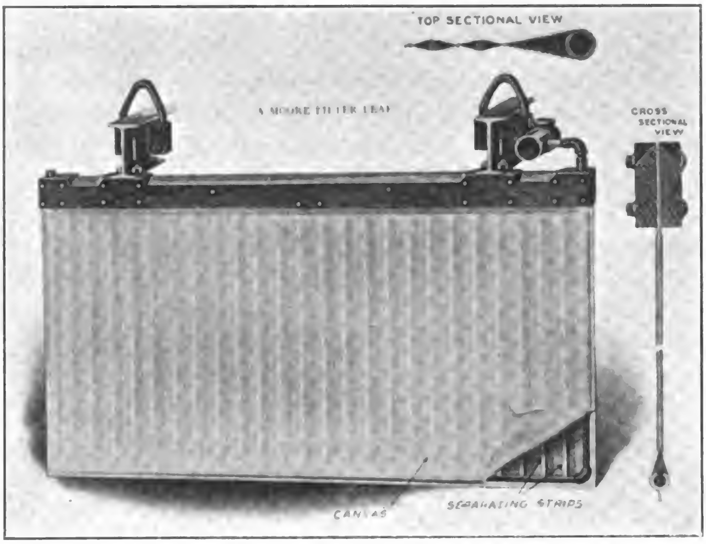
TOP SECTIONAL VIEW
CROSS SECTIONAL VIEW
SEPARATING STRIPS

Fig. 2.

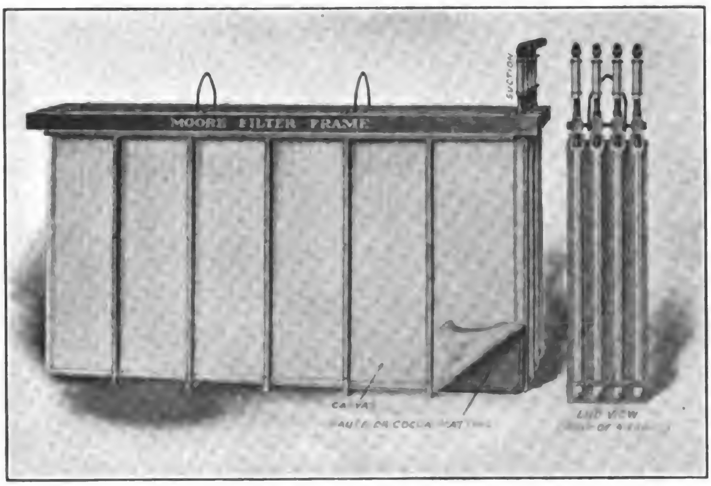
MOORE FILTER FRAME
SUCTION
END VIEW

Fig. 3.

are reinforced by means of rows of stitches and stiffening strips of wood which maintain the rigidity of the filtering medium when pressure or suction is applied. As shown in the illustration, one of the side tubes is connected by means of a flexible tube to the suction end of a vacuum pump. The leaves can be obtained in any desired size and are usually coupled to form a "basket" as illustrated by Fig. 3.

The operation of this filter is very simple. When the suction is applied after the "basket" is immersed in the effluent, clear liquid is drawn through the filtering medium, then through the

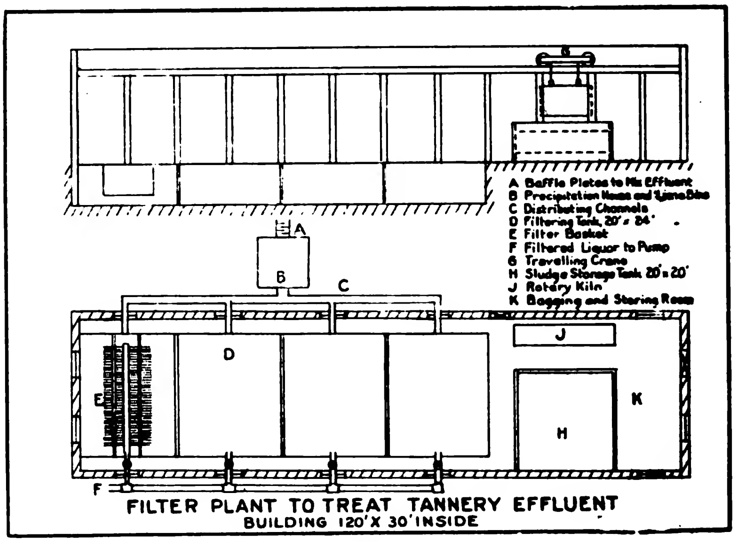

Fig. 4.

pipe shown, to the pump while a uniform cake of sludge deposits on the leaves. The filtering is continued while the effluent is kept agitated by a current of air, until a thickness of cake forms which hinders the action of the filter. The "basket" can then be raised by a traveling crane and it is kept suspended for a while with the suction still applied so that the moisture content of the sludge is reduced. The "basket" is then carried to a sludge tank where pressure is applied from within the leaves and the sludge is deposited leaving the basket ready to resume its action.

Fig. 4 shows a plan of a plant to handle one million gallons of effluent per day. The alkaline effluent enters at A where it is thoroughly mixed by baffle plates and then passes through B where the aluminium sulphate is added as in the plant previously described. The precipitated sewerage then passes into the tanks which are in operation, and as there is comparatively little sludge, a basket will probably operate well for one-half hour, with a continuous flow into the tanks, before it will have to be removed. The process of filtering and removal of the sludge from the leaves has already been described. The effluent coming from the pump should be fit to enter any sewer or stream without danger of contamination. The sludge contains forty or less per cent. of moisture, according as the length of time of application of the suction while the basket is suspended in the air. This sludge is collected in a tank and can be dried by the rotary kiln shown in the diagram, and the product can be bagged and sold to the fertilizer manufacturer for four to six dollars per ton.

Exclusive of the building and land, the principal cost for a plant of this sort will be for the baskets, traveling crane, and pumps. A plant treating one million gallons per day should have three baskets each of forty leaves and each leaf being ten by six feet. Two of the baskets should be in constant operation. The depreciation on this type of plant will be relatively large as the tanks will be made of wood and wear and tear on the pumps, baskets, and crane will be great. The cost of labor will be about ten dollars per day.

Although there will be a greater depreciation in this plant than the one employing settling tanks and the labor and upkeep cost will be greater with a consequent loss per day on the amount of sludge obtained as fertilizer, the initial cost of installing this plant will be smaller with consequent less investment charge and a more rapid, compact, and efficient system will be employed.

SUMMARY

This investigation has shown that the assumed great loss of hide substance in the tanning industry is not very great. It has demonstrated that nearly sixty per cent. of this loss can be recovered and prepared into a marketable product.

Methods of treating the effluent under varying conditions have been described, and although these methods may not be very profitable to the tanner, their use will eliminate a nuisance and will relieve the tension between him and the public.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

TANNERY REFUSE AS A FERTILIZER.*

By Henry W. Healy.

The refuse of tanneries that is available for agricultural purposes may be roughly divided into refuse material from the beam house, where the hides are prepared for tanning, and the ashes from the steam plant. There are three methods of preparing hides for tanning, but from only one, namely, that where the hair of the hide is loosened by submerging in strong lime water, is there a big product useful for agricultural purposes. Hides are submerged into large pools or vats with a large quantity of lime put in them. This lime, after being used for a certain length of time, becomes fouled with manure, hair and ammonia. When this condition arises the water is pumped out and the residue of solids in the bottom of the vats is thrown out of doors into large piles. These piles of lime are about as valuable per unit of lime as is lime in any form that is usually purchased commercially. Of course, it contains considerable moisture even after being exposed through a dry season, but to offset the moisture the refuse contains enough animal matter to the extent of three-quarters of one per cent. to two per cent. nitrogen. This material is very valuable to apply as a top-dressing to grass lands, as most grass lands need lime, and the available nitrogen can be utilized readily by the growing plants. If this refuse lime is applied to small grain, frequently the grain lodges, as there is an abundance of nitrogen and a lack of phosphorus and potash. On the other hand, when it is applied to land for corn, the nitrogen is utilized to good advantage and the lime remains in the soil for the grass or grain that may follow.

The other residue from tanneries is the ashes. Leather is

* Rural New Yorker, May, 1912.

tanned with a liquor that is made by running boiling water through finely ground bark of various trees, particularly hemlock and oak. When the tanning strength of the bark has been exhausted, this spent bark is used as fuel. In addition to this spent bark, it is usually necessary to use some coal, so that the ashes are not purely spent bark ashes, but also often contain coal ashes. Pure bark ashes analyzed show from three-quarters of one per cent. to 1½ per cent. potash and half of the quantity of phosphorus. On the other hand, the lime contained in the ashes is very high, running from 30 to over 50 per cent. The value of these ashes is reduced in proportion to the amount of coal ashes mixed in with them. A few tanneries do not use coal where hard wood is cheap, and, of course, these ashes are more valuable than the average. The reason why these spent bark ashes are so low in phosphorus and potash is because of the leaching, which removes the fertilizing value with the tanning material. Spent bark ashes are, like lime, best applied to grass or growing grains. A very convenient time to do this is in the Winter when the teams are idle and the ground frozen. The ashes may then be cheaply hauled and spread upon the land. I should say that if ashes can be spread upon the land at a cost of $1.50 a ton, a profit could be made by their use. The spent lime is, of course, valuable in proportion to the cost of lime at the farm where it was used.

I know of one farm in Northern Pennsylvania which was purchased by a man interested in a tannery. He bought a year's production of the refuse lime and ashes from a large tannery for less than $100. In the Spring he purchased a team of horses and hired one man to start hauling lime and ashes from the tannery to his farm, which was so run down that hardly anything grew. These were spread broadcast, and as soon as a field was completely covered, it was plowed and sown to grass, sometimes with a crop of small grain and sometimes without. He used clover, and the results obtained from this procedure were very astonishing. Many people who visited the farm could not believe that so great a change could take place in such a short time. The growth of grass and clover was well over two tons per acre in one cutting. This treatment has been carried on for a period of two years. Each Autumn the man was discharged and the team and

wagon sold, and another team bought and a man hired the following Spring. The growth of grass the second year beat all expectations, and it is thought there will be larger profits as the area of improved land increases. In addition to this there is the profit of the increase in the value of the land. Whereas it was worth but $5 or $10 an acre two years ago, the improved land is well worth more than $50 an acre now.

At another tannery located in Georgia, there is a large farm on the premises. It has been the practice at this place to spread the ashes on the field as fast as they are accumulated, and to run the lime water through troughs like irrigating ditches. This farm is about 75 acres, and has grown half of its area in corn every year. No fertilizer has been used except that produced at the tannery. The land is growing as much corn now as it ever did, the yield averaging about 60 bushels per acre. During the last three years a portion of the land has been planted to alfalfa, which thrives wonderfully, although the land is level and the drainage apparently poor. From the use of so much lime and ashes during the past years, the texture of the soil is such that there is a natural drainage to the subsoil far below the surface, which carries away the surplus rain water. Alfalfa in this section is cut five times a year and the total yield per acre is usually over five tons, and as this hay is sold in the neighborhood of $25 a ton, there is certainly a splendid profit.

The writer has seen tannery refuse used on as many as 20 different farms in localities ranging from Georgia to New York State and Wisconsin, and on hilly, clayey soil as well as level sandy soil. In every case there is a great improvement in the texture of the soil. If the land was inclined to be acid (and most eastern soil seems to be), the improvement, of course, was largely due to rectifying this condition. How much of this material may be used it is difficult to state. On one farm 80 tons of refuse lime was applied to two acres (the tannery was willing to spend money to get it out of the way). The growth of vegetation was enormous and no ill effects were noticeable. Ashes are frequently applied at the rate of 15 to 20 tons per acre to grass lands in the Winter. The most noticeable effect of the application of ashes is the increase in the percentage of clover.

The value of these tannery products is a matter for each farmer to investigate himself. If the hauling of them can be done in the Winter time with an otherwise idle team, the money is well spent. If, on the other hand, the tannery refuse must be loaded into cars, resulting in a freight charge as well as the cost of hauling from the railroad station, it may be questionable whether it would pay to use this material unless the land is in need of lime. Lime is furnished by both ashes and refuse lime. On the writer's personal farm, he has used the refuse lime alone to the extent of from three to 10 tons per acre, the object being to obtain a stand of alfalfa. In every case where it was applied, a thrifty stand of alfalfa resulted. Of course, the land was well prepared and the seed inoculated. A very good rule to determine the value of tannery refuse would be half the cost of quicklime delivered on the farm in barrels. I do not think that there would be quite half the available lime that there is in quicklime, but there is sufficient nitrogen to make up the difference in value.

In addition to the refuse lime and the ashes from the tanneries, there are many forms of liquids that have to be disposed of. After the liquors used for tanning leather have been largely exhausted, they must be run to a sewer of some kind. These liquors are frequently of no value agriculturally until they have been exposed to the air and allowed to rot. This decomposition is hastened if lime water is mixed with the liquors. Old liquors usually have a large amount of different kinds of acids which would be more or less injurious to growing plants. This acid, of course, would be neutralized by the lime water. When liquors mixed with lime water are run upon the soil, the land should be frequently harrowed or cultivated in order to aerate it. The liquors precipitate a slime on the surface which forms a crust and does not permit the roots of the plants sufficient air to thrive. I have seen old fields where liquids have been allowed to run and kill the grass, plowed up and planted to a new crop, and a very excellent yield often results because the surface deposit has become rotten in time. The acid is neutralized, when mixed with the soil, plant food seems to be liberated and the texture of the land improved. I have talked to agricultural chemists, who stated that there are often toxic poisons in the soil which are

injurious to plant life. One well-known chemist gave me as his opinion that tannery refuse lime was extremely valuable in overcoming these toxic poisons, and such seems to be the case, because I have known tannery refuse to be more valuable on some lands than on others, both in need of lime. The wornout hillsides of farms east of the Alleghany Mountains seem to respond best to applications of tannery refuse. I think this is due to their natural lack of lime and the poor texture of the soil. Without a doubt much valuable material is constantly going to waste that could be hauled to nearby farms at slight expense. The difficulty is that when demonstrations are made and the improvement demonstrated, the use of these materials is not continued. Perhaps the reason for this lies in the minds of the farmers themselves, *i. e.*, I know of one farming community that prefers timothy hay for feeding beef cattle in Winter to alfalfa at half the price. In general, tanneries are located in regions where farm lands are poor and the farmers unenlightened. The latter accounts for their failure to utilize a material so cheap, and it also accounts for the fact the farm lands continue poor and the farmers not prosperous.

ABSTRACTS.

Swelling of Gelatin in Aqueous Solutions. R. Ehrenberg. *Biochem. Zeitschr.*, 1913, 53, 356-90. The author has carried out and tabulated the results of a large number of experiments upon the swelling of 10 and 20 per cent. gelatin jellies in water and in various aqueous solutions. The relative effect of different electrolytes on the swelling varies according to the concentration, *e. g.*, in concentrated solutions sodium sulphate is less active than sodium chloride, and may even produce contraction, but in dilute solutions (less than 0.2 *N*,) it is more active. If the salts are dissolved with the gelatin in making the original jelly, they diffuse out and behave in the same way as they would if originally dissolved in the outer solution. On the basis of these and other results, the author believes that the swelling is not caused by a single process, but by two or more, and that a particular effect may preponderate according to circumstances. The whole process certainly cannot be explained on osmotic grounds, though osmotic phenomena are not excluded. Probably electro-endosmose may play a part, the gelatin being enclosed by a polarizable membrane and the electromotive force coming from diffusion or membrane potentials. W. H. P. in *J. S. C. I.*

Chrome Leather Manufacturer in Southern India. Consul Henry D. Baker, *Daily Consular and Trade Reports.* The manufacture of chrome leather, in which various compounds of chromium instead of vegetable tanning materials are used, is making rapid progress in various parts of India, especially in the Madras Presidency and in the native State of Mysore, where the respective Governments by painstaking official efforts, and the introduction of machinery from the United States for experimental purposes, pioneered the industry into a position which has subsequently prompted the increasing investment of private capital.

In 1903, the Government of the Madras Presidency, in order to improve the conditions in the tanning industry, began experiments in chrome tanning on American lines, and these were so successful as to lead to the establishment of a Government Chrome Tannery, to serve mainly as an object lesson to encourage investment of private capital. After the establishment in 1910 of two large private chrome tanneries in the south of India, the Government factory was sold, it being then considered an accepted fact that the possibility of manufacturing chrome-tanned leather in India on a commercial scale had been sufficiently demonstrated.

The original idea of the Director of Industries of the Madras Presidency in carrying on this work at first at the Madras School of Arts, was to manufacture water bags or "mussacks," "mhotes," "kavalais," or "chursas," as they are called in different parts of India. In India the largest demand for leather is for water bags, or "mhotes," of which many hundred thousands are required every year, and for each "mhote" two good hides are used up. To supply the sandals required by nearly 300,000,000 people, a very large quantity of leather is also used, and for both these classes of goods chrome leather has been found by the natives to be eminently suited to their requirements. It was soon found that there was no difficulty in doing this, and that in fact it was possible to carry the original idea much further, as the leather proved equally suitable for practically all purposes for which it is usually employed. Dyeing and leather dressing were therefore taken up and finished leathers are now made suitable for harness, saddlery, boots and shoes, sandals and slippers, belting, washers for cottoning rollers, and a great variety of other industrial purposes.

Chrome-tanned leather is in every way a superior material to any that has hitherto been produced in India, and in many respects it has great advantages over the very best imported leather. Water has very little effect upon it and chrome leather which has been wetted is just as soft when dried as before, and as a material for boots and gaiters this advantage is a very important one. It is well known that ordinary leather is rapidly destroyed when subject to different alternations of wetting and drying, which are so common in India. The ordinary leather in India becomes hard and cracks, whereas chrome leather, remaining soft and pliable, is unaffected by such treatment. Compared with bark leather, chrome leather is soft and well adapted for boots and shoes, while by a special

process, sole leather can be prepared from it which is extremely durable.

In the native State of Mysore tanning is one of the most important industries, the annual turnover averaging about $3,350,000, and there is even an important export business of tanneries in Bangalore to Europe by way of Madras. Three years ago a small company was started at Bangalore to manufacture chrome leather, the manager having been trained in the industry at the Madras School of Arts, and then in the Madras Government Chrome Tannery. The Government of Mysore became interested in this tannery to the extent of one-third of the capital subscribed and has given it still more important assistance by extending to it the patronage of the various Government departments which require leather in one form or another. The factory is well equipped with modern American machinery, and has recently been increasing the equipment for its business. It turns out chiefly, but not entirely, chrome leather, of which it sells about $4,000 worth per month.

An interesting feature of the chrome leather establishments in southern India is the preparation of hunters' animal trophies, chiefly tiger skins, of which some excellent specimens occasionally are brought in. There has also been some attempt to enter into the commercial tanning of snake skins, chiefly for belts, card cases, ladies' hand bags, etc. It has proved too difficult, however, to obtain the snake skins in sufficient quantities, for while statistics of India show that nearly 25,000 people die of snake bite every year, and while nearly 100,000 snakes are killed every year, chiefly in response to Government payments for their destruction, yet there seem to be few persons disposed to systematically hunt out and gather in the dangerous snakes of the country for any commercial reward offered, and when snake skins are offered at the tanneries the price is usually about $1.50 per snake, which is too high to permit of much commercial profit in preparation of the skins.

Chromium, the compounds of which are used in the chrome leather industry, is a mineral which is rather plentiful in Mysore, and new deposits are frequently found. The most important chromium mine is at Tiptur, about 90 miles from Bangalore. The present chromium production in the State is about 2,600 tons annually.

In the Madras Presidency the latest census returns show that in 1910-11 raw hides and skins, chiefly those of goats, sheep, buffaloes, and bullocks, amounted to 106,562 hundredweight (hundredweight = 112 pounds) for use by the tanneries for export trade, the tanned hides and skins amounting to 242,060 hundredweight. In 1901-02 the similar production of tanned hides and skins amounted to 224,864 hundredweight from 87,049 hundredweight of raw hides and skins. There are now about 15,000 persons engaged in the manufacture of leather in this Presidency, a gain of nearly 50 per cent. within the last decade. The number of persons, however, engaged in the manufacture of leather articles has decreased within the last decade from 50,795 to 37,028. This decrease has been due partly to the rise in value of leather, which has

led to its being replaced by iron as the material from which buckets are made, and also to the concentration of such industry in factories, where work is now accomplished by machinery which was formerly done by hand by numbers of persons in the various villages. There has, however, been a gain of over 10 per cent. during the last decade in the number of boot, shoe, and sandal makers, who amounted in 1911 to 123,253 in number.

Previous to 1898 the export of raw hides from southern India was insignificant, but with the new tariff schedule, established in the United States during that year a large demand for raw skins came from American tanners. The declared exports from Madras to the United States during the calendar years 1910, 1911, and 1912 were as follows:

Skins	1910 Number	1911 Number	1912 Number
Calf—			
Dry	——	184	——
Pickled	309	13,918	30
Goat and sheep—			
Dry salted ...	345,759	487,653	496,194
Pickled	10,784	181	14,881
Tanned	659,541	644,720	854,764
Wet salted ..	263,246	10,936	17,169
Tanned cowhides ..	14,715	247	——
Hide fleshings	55,571	61,043	124,804
Total	1,329,925	1,218,882	1,507,842

Practically the whole of the leather export trade from Madras is in tanned hides and skins and not in finished goods. The hides and the skins are tanned but not dressed. Hide tanneries are generally much smaller than those devoted to skins. The capital outlay involved in setting up a tannery, even of the largest kind, is not much, and there are numerous small tanneries in which a few hundred dollars will probably cover the whole cost. As a natural consequence work is carried on in the tanneries very irregularly, all the more so as the tanners themselves have generally very little capital, and are almost entirely dependent upon advances from the export merchants where-with to buy skins or hides to carry on their business. The most recent returns from the inspector of factories of India show that out of 18 tanneries in India employing over 50 hands, 14 are situated in the Madras Presidency, but all the Madras tanneries are small compared with those situated at Cawnpore, and at Sion, near Bombay.

The chrome leather industry which now employs the best machinery and produces the best article has to depend at present almost entirely on local consumption for its market, as the fiscal regulations of most countries prevent profitable export from here of finished leather.

Oak Extract. U. J. THUAU. *Le Cuir*, VI, 595-8. Sept. 1, 1913. Oak extract, as the term is commonly used in Europe, means extract of oak wood, not bark. This extract is not much made in France. On account of its high sugar content, unless special precautions are taken, it is liable to fermentation. When properly made and clarified this extract makes the best material for vat tannage, because it furnishes to the leather a natural swelling agent. For drum tannage, it may be to advantage mixed with an equal quantity of chestnut extract. Chestnut tannin is of the pyrogallol class, while oak is a mixture of pyrogallol and catechol. The penetrating ability of the oak extract is due to the catechol tannin. The two extracts are easily identified by chemical tests, but in spite cf this fact chestnut extract or a mixture of chestnut and oak is sold under the name of oak. One reason for the failure on the part of tanners to realize the value of oak extract is the practice of makers in extracting the wood under pressure in order to obtain a high yield. The pressures used range up to two or three atmospheres, with temperatures up to 130° C. (266° F). Extract made from liquor extracted under pressure has more non-tannins than that made from liquor extracted in the open. That is to say, a pressure extract of a given degree Baumé has less tannin than an open extract of the same degree. At temperatures above the boiling point, most tannins begin to decompose, either into pyrogallic, gallic and ellagic acids, or into anhydrides of tannins (phlobaphenes) or into glucose. Extraction under pressure takes from the material both more tannin and more non-tannin, and also converts some of the tannin into non-tannin. The following table shows analyses of both chestnut and oak extracts of 25° Baumé, one sample of each made from liquor obtained by open extraction, and the other from that obtained by extraction in autoclaves under pressure.

	Chestnut		Oak	
	Open Per cent.	Pressure Per cent.	Open Per cent.	Pressure Per cent.
Tannin	32.0	29.8	31.3	26.5
Non-tannins	7.3	12.0	8.2	14.0
Insolubles	0.0	0.0	0.0	0.5
Water	60.7	28.5	60.5	59.0

The difference between the two extracts is greater in the case of the oak, not only in the analytical results, but also in the practical working. The excess of non-tans in the pressure extract consists in the case of the chestnut chiefly of anhydrides of tannins, while in the case of the oak it is mainly composed of glucose and glucosides, which cause a tendency to ferment. In order to obtain an extract with the lowest non-tans, the extraction of the wood should be carried out at temperatures not exceeding 85° C. (185° F). In order entirely to prevent fermentation, the maker may with advantage add sodium fluoride to an amount equivalent to 0.3 per cent of the weight of the extract.

A good oak extract dissolves easily in cold water, with little residue. It gives to the inner part of the leather a dark color, so that if one cuts

a leather tanned with oak and chestnut half and half, the color of the cut edge is darker than that tanned with chestnut alone. The extract itself is lighter in color than chestnut. It gives a beautiful yellow color to the grain, penetrates rapidly and makes firm leather. L. B.

Extraction of Tanning Materials. E. GIUSIANA. *Le Cuir,* VI, 611-13. In the effort to secure the most complete extraction possible, it has become customary to use copper autoclaves, and the liquors thus extracted under pressure are inferior in color to those leached in open vats, and also contain more or less undesirable material, consisting of resins, etc. Liquors obtained in open leaches are not so high in density as those leached under pressure. Dr. Giusiana proposes to make use of the well-known fact that movement promotes diffusion, to obtain strong liquors and close leaching. He proposes to put the material to be leached into revolving drums, arranged in batteries in the same manner as ordinary leaches. He expects this system to show several advantages. Extraction could be carried out at a temperature low enough to avoid the disadvantages of the autoclave system. The time required would be less than at present. The liquors would be lighter in color. L. B.

Factors which Influence the Yield of Leather. J. R. BLOCKLEY. *Leather World,* V, 548-9, 623-4. Three factors are recognized: 1, as little loss as possible in the soaks and limes; 2, keeping the hide while being tanned in the most favorable condition for the absorption of tan; 3, use of the right tanning materials. Experiments in the Leathersellers' College show loss in the soaks for fresh hides 0.48 per cent. and for dry hides 1.73 per cent. The loss in ten days' liming, three pit system, was 1.10 per cent. In order that the yield may be good, the hides must be kept plump in the liquors. That this may be the case, the liquors must be acid. Experiment illustrating this point: Pieces of delimed pelt as uniform as possible were divided into 4 packs and tanned in similar liquors. To the liquors of pack A no acid was added, to those of pack B 1/10 per cent. acid was added, to those of pack C 1/2 per cent. and to those of pack D 1 per cent. was added. The table shows the amount of tannin absorbed per 100 parts of hide substance.

	After 6 days	After 21 days	After 70 days
Pack A (no acid added)	6.5	57.2	111.5
Pack B (0.1 per cent. acid added)	8.3	61.3	132.0
Pack C (0.5 per cent. acid added)	12.0	67.2	136.0
Pack D (1 per cent. acid added)	23.6	76.1	140.0

With reference to the third factor, Mr. Blockley quotes the results of Youl and Griffiths and of Paessler, which have been pretty fully discussed by R. H. Wisdom, in connection with his own results, in his paper in the June number of this Journal, (pages 232-6.)

Nitro-cellulose and its uses in Leather Finishing. M. C. LAMB. *Leather World,* V, 272-3, 357-8, 368-70. Nitro-cellulose, (also called gun-

cotten, soluble cotton, collodion cotton and pyroxylin,) is made by treating cotton with a mixture of nitric and sulphuric acid. When dried it looks much like the original cotton. It is explosive, and is soluble in various organic solvents, that most often used in preparing leather varnishes being amyl acetate. The film left when the amyl acetate evaporates is hard and transparent. Benzol and wood alcohol may be used to dilute solutions of nitro-cellulose, though these are not solvents by themselves. More than 100 kinds of soluble cotton can be made by varying the acid mixtures, the temperature of the reaction and the length of time the process is continued. Some of these sorts are much better adapted for making leather finishes than others. In using benzol to dilute cotton solutions, care must be taken not to use too much benzol, or the cotton will be precipitated. If a solution of soluble cotton be added to the linseed oil varnish used in japanning, the gloss is increased, and the varnish is more elastic. With this mixture it is possible to make patent leather from chrome tanned stock. Nitro-cellulose solution may also be used in the manufacture of enamelled splits for furniture covering, and for automobile leathers. Such a solution applied to the sweat band of a hat makes it waterproof, and fixes the color. A weak solution applied to morocco goats prevents the dye from rubbing off. For enameling flesh splits, dissolve from 8 to 10 ounces of nitro-cellulose in 3 pints of amyl acetate, and dilute to 1 gallon by adding a mixture of equal parts of benzol and alcohol, in which 8 ounces of castor oil have been dissolved. Stir in fine-ground pigment until the mixture has the consistency of paint. The oil is to render the film pliable. A larger amount of castor oil makes the film more pliable, but less glossy. Apply rapidly with a brush and dry in a warm place. Apply a second coat with less castor oil, and dry again. When a bright finish is desired, a third coat is added, consisting of a 4 per cent. solution of nitro-cellulose to which a little boiled linseed oil has been added, but no pigment. Enamels containing soluble cotton, beside the advantages already mentioned, may be dried at a lower temperature than linseed oil finishes alone, and without exposure to sunlight, and they may be transparent, thus showing the grain of the leather. The linseed oil to be used in making the mixed enamel should be free of adulteration and should be stored in lead lined tanks for several years before boiling, to allow the mucilaginous matter to settle out. Oil so stored gives a more glossy varnish than can be made with new oil. The oil to be boiled is placed in a large iron pan, and after heating for two hours, a small quantity of finely ground mixed burnt umber and Prussian blue is added. The boiling is continued until the oil has the consistency of a thick syrup. When it has cooled to about 130° F, to each 25 gallons of oil are added 5 gallons of benzol in which 2 pounds of nigrosine has been dissolved, the solution being added slowly with constant stirring. The mixture now stands several days, and is strained through a fine linen cloth before use. The nitro-cellulose solution, made by dissolving the cotton in amyl acetate and diluting with benzol and

alcohol, should have a strength of 5 or 6 per cent. The leather to be japanned should be free from grease. It is sufficient to rub the grain of goat or calf with kerosene or benzine and let it dry. Sheep must be degreased with benzine or other solvent. In fat-liquoring, use castor or cottonseed oil, as little as possible consistent with securing the necessary pliability. Stretch the goods on boards or frames, and dry at 90° F. Any small holes may be stopped by pieces of adhesive cloth applied to the flesh side. For the first coat, use two parts of the cotton solution to one of boiled linseed oil. The mixture is heated to 93°-95° F, and applied with a "raclette," a slightly toothed sleaker, in a room at 90° F. The atmosphere in the room must be dry, as the japan may otherwise absorb moisture, precipitating the cotton and making the coating opaque. The enamel is applied warm so that it may be easily spread. If it were diluted to secure the same degree of thinness, it would penetrate further into the leather than is desirable. After the first coat is on, the skins are placed flat in the drying room whose temperature is 95° F. After drying, the surface is pumiced, to remove any small lumps, and roughen the enamel so that the next coat will stick better. The second coat may have one part of oil to four of the dissolved cotton, and is applied with a flat varnish brush. It is important to brush on the varnish quickly, and each coat should be as thin as possible. After drying again, a third coat is applied, with a still smaller proportion of oil. Many makers put on a fourth coat, which should have not more than one tenth as much oil as cotton solution. Nitro-cellulose solution is preferable to shellac for waterproofing hat leathers because it does not give the yellow tint caused by shellac. Collodion varnishes are also used in giving a gloss finish to pocket books and fancy leather goods.

The Catalytic Action of the Colloidal Tannins as Oxygen Carriers (Pseuo bacteria). E. O. SOMMERHOFF. *Collegium,* 1913, pp. 416-20. The oxidation of wet hide by the air doubtless plays a great part in tannage; the generation of heat during the process confirms this. Tanning experiments in a shaker in a vigorous current of air and in closed vessels in an atmosphere of CO_2 showed the retarding influence of the latter, the hide not losing its swelling power so rapidly as usual. The tanning process is assumed to include an oxidation of the hide together with splitting off of water, the absorbed tannin acting as a catalytic substance for oxygen. The oxidized colloidal albumins differ from the original albumins of the green hide in having lost much of their capacity for swelling.

The author extends his theory* of bacterial colloids and two forms of colloidal albumin to all colloids, and especially vegetable tannins. The catalytically active (oxygen-carrying) tannin colloids are regarded as analogous to living bacteria and the inactive to dead ones. Summing up his speculations he distinguishes (1) tannin colloids which are absorbed

* Abstr. ante, p. 412.

by the hide during oxidation (virulent colloids), good tannage, (2) tannin colloids absorbed without oxidation (coagulated or dead colloids) poor tannage. The greater the number of well tanned alpha albumins of the hide, the better the resistance to water, etc. (in the cold). Tan-wood extracts should have (1) high colloidal power ("body"), acting like a well boiled glue; (2) on rapid dilution should separate light, not resinous phlobaphenes; (3) should give a good permanganate titer (Löwenthal) indicating capacity for oxygen; (4) should possess a good decolorizing power towards hide indicating capacity for transferring oxygen to the albumins; (5) and should be analyzed for ash and sulphur; the tannin content of sulphite cellulose determined by hide powder probably consists largely of colloidal sulphur which in presence of other colloids goes through all filters and then tans (pseudo-tannin).

It is better to ignore the tannin analysis by the hide powder filter method. The charging effect of an extract can only be determined by factory practice. W. J. K.

Soaps from Sulphonated Oils. A. Chaplet. *Rev. de chimie industrielle* through *Les mat. grasses,* 1913 (6), 3206-8. By action of conc. H_2SO_4 at ordinary temperatures upon fatty acids a sulphonated derivative is formed; in the case of a glyceride there is produced in addition a sulpho-acid of glycerol which gives with water glycerol and H_2SO_4. The theory of the reactions has been studied but is not clear nor does this have much practical bearing upon the manufacture of these soaps.

The choice of oils for sulphonation is important. Castor oil is mostly used since it gives the most soluble soaps; also the residual oleines separated from stearine are used. If a colorless product is required, it is indispensable to use oil from the first pressing containing a minimum amount of gums and impurities which brown with the H_2SO_4. For manufacture upon a simple scale wooden vats are used, the H_2SO_4 being fed through a small lead pipe and agitated by revolving paddles worked by a crank. As wood is a bad conductor, it is important to interrupt the flow of acid on development of too much heat. Vessels of stone or porcelain are also used. According to Belter, to 100 kg. of castor oil 26 kg. colorless H_2SO_4 of 66° B. are gradually added. The initial temperature of the constituents should not exceed 15° and the final temperature remain about 30°. The reaction should not generate bubbles of SO_2 during the constant stirring; the flow of acid consumes 8-10 hours. The oil is let stand 12 hours, then washed in stages with luke-warm (40°) water containing 15 kg. salt to the total 500 liters. The last wash water ought not be acid to litmus paper. These proportions give a completely sulphonated acid, while a partially sulphonated acid is obtained by using 18, 13 or 9 kg. H_2SO_4, giving less soluble soaps.

On the industrial scale large vessels of sheet iron lined with lead are used, jackets for cooling water. Sometimes an air current is used for agitation. According to M. Ehrsam, 20 per cent. of H_2SO_4 is used for

oil of first pressing, 25 per cent. for second pressing oil and 30-40 per cent. for oleine. The oil is agitated at 20° and the acid added with agitation maintaining the temperature below 35°. The sulphonated oil is finally washed in a separate vat first with plain water, then with 10 per cent. salt. The final product is 110 kg. sulphonated oil for 100 kg. castor oil, $C_{17}H_{32}\left\{\begin{matrix}OH\\COOH\end{matrix}\right.$ converted into $C_{17}H_{32}\left.\begin{matrix}OSO_3H\\COOH\end{matrix}\right\}$. The principal so-called sulpho-oils prepared by the above method are alkaline sulpho-arachidates, sulpholinoleates and sulphooleinates.

In the manufacture of the soap "Monopol" by Stockhausen at Crefeld which is valued because it is not pptd. by lime salts, the above sulphonation is followed by heating. A glyceride oil is added and the cooled mixture sulphonated anew. The process is patented and in part secret.

Neutralization. Caustic soda at ordinary temperature is used for sulpho-oil intended for dressing and ammonia for that used in dyeing. To avoid an injurious excess of soda one may finish with ammonia which also serves to correct incomplete washing. For 100 kg. oil, about 10 kg. ammonia 22°B., or 20 per cent. soda lye of 36° B. are needed, giving permanent liquid products; above 80 per cent. purity the products are gelatinous and inconvenient to use. W. J. K.

Difficultly Soluble Tanstuffs. W. Moeller. *Ledertechn Rundschau.* 1913 (5), 258-9. This article is called forth by Sommerhoff's recent paper on tannage with insoluble metallic jellies. He has before expressed the view that the phlobaphenes present in natural untreated quebracho are important in tannage and that it is a damage to the extract to remove them. The tanning process in general is most satisfactorily explained from the colloido-chemical standpoint. Procter, von Schroeder, Eitner, Bögh and Fahrion agree in crediting the phlobaphenes with more or less tanning power. There is no definite clarity in a colloidal solution which explains the variable results obtained by analysts in determining insolubles by the usual method. On preparing solutions of analytical strength, the phlobaphenes separate in part, are filtered off and reckoned with the insolubles. It is desirable that in the case of warm soluble extracts, the insoluble genuine non-tans be distinguished from the difficult soluble tans. The ratio of insoluble tans to soluble tans in natural quebracho extract is about 1:10 at analysis strength; it increases with further concentration, reaching 2:3 at 8-10°B but on continuing the concentration the insolubles dissolve and the solution is complete at 20° B.

The author has attempted to work out a method for the determination of the difficult soluble tans without so far satisfactory results. Experiments were made in filtration of liquors of analysis strength in a hot water funnel at 98-100°. The filter had previously been tanned with the solution, washed with warm water, dried and weighed. A measured (cold) amount of the solution was next filtered hot until it remained clear at 100°. The filter was then dried and weighed the increase giving insoluble non-tans. By another indirect process, the filter was foretanned one hour

in the hot funnel with a measured quantity of liquid. After the filter was freed from the liquor, a new portion (measured cold) was filtered through hot until permanently clear (hot). The filtrate is made up to original volume, having lost by evaporation, and 50 cc. evaporated to dryness. The difference in weights of this residue and total residue = insoluble non-tans. Although the author obtained no uniform results, he regards the method as the only rational one and worthy of careful trial in a research laboratory. W. J. K.

PATENTS.

Machine for Treating Leather. U. S. Patent No. 1,073,064. GEO. V. ANDERSON, Philadelphia, Pa.

Leather for Pneumatic Tires. English Patent, No. 11,034. E. RINGEISEN, Plaine St. Denis, France. Hide is degreased with ammonia, reduced to the proper thickness and then hardened by immersion in a 3 per cent. sulphuric acid solution. After drying it is coated with glue.

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TENTH ANNUAL MEETING.

The Tenth Annual Meeting of the American Leather Chemists Association will be held at Atlantic City, New Jersey, Dec. 4, 5 and 6, 1913. The committee having in charge the arrangements for the meeting has selected Hotel Traymore as the place of meeting. A suitable room has been reserved for the meetings, and members who desire to retain rooms at the hotel are requested to apply directly to the management as early as possible. The following is the schedule of prices:

OLD BUILDING.

One person, $4 or $5 per day, without bath.
Two persons, $8 or $9 per day, without bath.
One person, $6 per day, with bath.
Two persons, $10 or $11 per day, with bath.

NEW BUILDING.

Each room with separate bath.
One person, $7 to $13 per day.
Two persons, $12 to $16 per day.

In addition to the reports of the officers and committees, the program will include the following:

Address, "The Use of Ozone in the Tannery," by Allen Rogers, Ph. D., Director Pratt Institute, Brooklyn, N. Y.

Address, "Detection of Mangrove in Admixture with Other Tanning Materials," by George A. Kerr, of the John H. Heald Co., Lynchburg, Va.

There will also be a paper on some subject of interest by J. J. Desmond, of the J. W. & A. P. Howard & Co., Corry, Pa., one or two papers from gentlemen in the Department of Agriculture, Washington, D. C., as well as other papers, announcement of which will be made later.

H. C. REED, *Secretary*.

REPORT OF COMMITTEE ON REVISION.

Owing to the careful and exhaustive revision which the official method of tannin analysis received at the hands of last year's Committee and the negligible amount of data published during the past year bearing on the method, this Committee has been obliged to consider comparatively few changes in the method as it now stands. The following list contains suggested changes as found in the report of last year's Committee on comparative extract analysis,—in the discussion of the report at the meeting,—and in a further discussion at a meeting of the Council,—so far as such have come to the attention of the Committee; also such other changes as the Committee felt needed consideration. Appended to each suggested change is the comment of the Committee.

Article 4.—Widen limits to .35-.45.

A return to the specifications before the revision: a step backward, not warranted by experience with the revised requirements.

Article 6.—Permit the use of half quantities for analysis.

Necessity not shown and believed by Committee likely to lead to greater inaccuracies and wider variations.

Article 7. A—Make the use of stoppered weighing bottles compulsory.

Evidence to date not sufficiently conclusive to warrant insistence on this point.

When dissolving the extract, add water at 85° C. to the flask before washing in extract.

No experimental evidence to show necessity. On other hand it involves no extra labor, is already practiced by many members and so is recommended by your Committee as possibly leading to slightly better uniformity of practice.

Article 7 A-a.—The solutions to be cooled by the rapid process shall stand in air one hour before being put in water and shall be agitated while cooling in water.

No evidence offered. Believed would require needless extra attention and labor from the analysts, be difficult of definition to secure concordant practice and not calculated to lead to as satisfactory agreement of results as present specifications.

Article 10.—Filtration shall be at 25° C. instead of 20° C.

A more radical change than is warranted by present analytical conditions.

Article 12.—Omit "woolly texture."

No better phraseology offered to characterize the fluffiness which seems a necessary property of a satisfactory hide powder; —so retained.

Define a method for determining the acidity of hide powder.

A necessary corollary of the acidity-limiting specification. No thoroughly satisfactory method for this determination having been found your Committee have recommended the adoption of a neutralization value obtained by averaging the acidities as estimated by the methods commonly known as Hough's and Small's, respectively. The acidity as found by Hough's method is likely to be low, by Small's high; an average seems more

likely by compensations of errors and of variations of practice to secure a reasonable agreement among analysts.

Article 12-*a*.—Forbid excessive kneading of the hide powder during the washing process.

Adopted. Data submitted showing excessive kneading gelatinizes hide powder and results in overlarge absorption and abnormally low non-tannin percentages.

b.—Define more exactly the method of rapid chroming.

Data submitted showing variations in time of preliminary soaking and of chroming lead to slight variations in non-tannins. Procedure recommended found of those tested to give results most in accord with the overnight chroming specified in *a*.

Require the analysis solution to be at 20° C. when the non-tannin determination is started.

No evidence. Believed unnecessary.

Specify some limits for the permissible speed of rotation of the shaking device.

Data submitted shows non-tannin values vary slightly with speed of rotation. Believed necessary to standardize the shaking device and provision for this is recommended.

Article 20.—Permit somewhat more latitude in the time of drying.

The original investigations on the drying of residues in the combined evaporator and dryer having shown little or no change in the weight of the residue after a sixteen-hour drying period, it is believed safe to broaden the drying specifications as recommended.

The following, therefore, are the changes in the present official method of tannin analysis recommended by your Committee.

Section 7-A. Par. No. 1.

Change the last sentence to read as follows:—Dissolve the extract by pouring into a liter flask approximately 400 cc. of water at 85° C., then washing in the extract with water at this temperature until the total volume is 900 cc., and finally rotating the flask gently by hand until a uniform solution is obtained.

7-B. Par. No. 1.

Change the last sentence to read:—So soon as such solution is obtained it shall be washed into a liter flask precisely as called for under 7-A.—Fluid Extracts.

Change the "Note" to read as follows:—It is permissible to make up 2-liter instead of 1-liter solutions, dissolving by pouring approximately 400 cc. of water at 85° C. into the 2-liter flask, then washing in the extract with water at this temperature until the total volume is 1,800 cc. after the manner specified above.

Substitute for Sect. 12 the following:

Section 12.—NON-TANNINS:

The hide powder used for the non-tannin determination shall be of woolly texture, well delimed, and shall require between 12 and 13 cc. of N/10 NaOH to neutralize the equivalent of 10 grams of the absolutely dry hide powder when tested as follows:

Weigh accurately in a 200 cc. Erlenmeyer flask approximately 6 grams of the air-dry powder, the water content of which is known. Add 100 cc. of boiling water and heat five minutes on a steam bath; add 1 cc. of phenolphthalein and titrate with N/10 NaOH, stoppering the flask and shaking vigorously after each addition of NaOH as the end point is neared. Take as the titration value the smallest amount of NaOH giving a pink lasting for thirty minutes in the stoppered flask after shaking vigorously for one minute.

To another similar accurately weighed portion of hide powder in a 200 cc. Erlenmeyer flask add 100 cc. of water and an accurately measured amount of N/10 NaOH between 1 and 2 cc. in excess of the titration value found above. Let stand one hour, the flask being stoppered. Titrate back the excess of alkali with N/10 HCl, shaking vigorously after each addition of acid. Take as the titration value the smallest amount of HCl, giving a mixture in the stoppered flask to which no pink returns in thirty minutes after shaking vigorously for one minute.

The neutralization value of the hide powder shall be considered to be the average number of cc. of N/10 NaOH,—calculated from the above two determinations—which would be required to neutralize 10 grams of the absolutely dry hide powder.

The hide powder shall be prepared for use as follows: either

(*a*) Digest the hide powder with 10 times its weight of distilled water till thoroughly soaked. Add 3 per cent. of chrome

alum ((Cr_2SO_4) $4K_2SO_424H_2O$, in 3 per cent. solution) calculated on the weight of the air-dry powder. Agitate frequently for several hours and let stand over night. Pour on cloth, drain, squeeze, and wash by digesting with 4 successive portions of distilled water, each portion equal in amount to 15 times the weight of the air-dry powder taken. Each digestion shall last for fifteen minutes and the hide powder and water be stirred or otherwise agitated occasionally during the digestion. Kneading or other excessive working of the hide powder in the water during the digestion is not permissible. After each digestion, except the last, the hide powder shall be squeezed to contain approximately 75 per cent. of water, a press being used if necessary. Or

(*b*) Digest the hide powder for 30 minutes with the amount of water specified under *a*, then add the amount of chrome alum in solution called for in *a* and agitate vigorously in some form of mechanical shaker for one hour. Proceed at once with the washing and subsequent operations precisely as specified under *a*.

The wet hide powder used for the analysis shall contain as nearly as possible 73 per cent. of water, not less than 71 per cent. nor more than 74 per cent. See Note.

Determine the moisture in the wet hide powder by drying approximately 20 grams. (See IV.)

To 200 cc. of the analysis solution in a 32-ounce wide mouth bottle of approximately 3½ inches diameter and 8½ inches height add such quantity of the wet hide as represents as closely as practicable 12.5 grams (not less than 12.2 nor more than 12.8) of absolutely dry hide. Immediately place the tightly stoppered bottle in a shaking machine so constructed that the bottle will rotate in a plane perpendicular to the axis of rotation, —the center of the bottle being approximately 3½ inches distant from the axis,—at a speed of between 60 and 65 revolutions per minute. Shake 10 minutes. Immediately pour the mixture on clean linen cloth, squeeze, and to the detannized solution add 2 grams of kaolin (answering the test described under (9)). Filter through a single folded filter (No. 1F Swedish recommended) of size sufficient to hold the entire filtrate, returning

until clear. Pipette 100 cc. of filtrate into a tared dish, evaporate and dry as in (8).

Funnels and receiving vessels must be kept covered during filtration. Flasks graduated to deliver 200 cc. are recommended for measuring the analysis solution to be detannized.

The weight of the non-tannin residue must be corrected for the dilution caused by the water contained in the wet hide powder.

Note: In order to limit the amount of hide powder used, determine the moisture in the air-dry powder and calculate the quantity equal to 12½ grams of actual dry hide powder. Take any multiple of this quantity according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing as nearly as possible 73 per cent. of water. Weigh the whole amount and divide by the multiple of the 12½ grams of actual dry hide powder taken to obtain the weight of wet hide powder for 200 cc. of solution.

IV. (20) EVAPORATION:

Change the last sentence to read: "The time for evaporation and drying shall be at least sixteen hours, and shall be as nearly exactly sixteen hours as practicable.

FRITZ H. SMALL, *Chairman*,
JNO. H. YOCUM,
H. C. REED.

A PRACTICAL METHOD OF RECOVERING GREASE FROM HARNESS LEATHER SCRAP.

By Philip McCutcheon Armstrong.

In every harness leather tannery there is a good deal of waste matter containing a large amount of grease. This scrap includes such things as buffings, whitenings, trimmings, table grease, floor scrapings, etc. In a few tanneries some sort of an attempt is made to recover the more valuable scrap, but in the majority of cases it is either burned or sold for a nominal sum to people called degreasers, who are in the business of recovering grease, and are equipped to do it on a large scale. The methods used by these degreasers usually depend upon the use of organic sol-

vents for grease, such as naphtha, benzol, gasoline, carbon tetrachloride, etc., and it is impossible entirely to remove them by distillation, so that the recovered grease invariably contains a portion of the solvent. As these solvents are all more or less injurious to leather, it follows that the grease recovered in this way cannot be used safely as stuffing by the harness tanner. In any case the necessary equipment is very costly, so that it would not pay the tanner to install it, for the comparatively small amount of stock he has to handle.

It is possible, however, to recover a very large percentage of the grease by means of a comparatively inexpensive apparatus, and so realize a great deal more than the scrap would bring if sold to the degreaser. Moreover, the grease recovered by the method we are about to describe contains no solvent matter at all, and is perfectly suitable to be used over again in the stuffing mill. If proper care be exercised the resulting grease is perfectly clean, and can be used perfectly safely mixed with the regular stuffing. In fact, for some unknown reason, this recovered grease enters the leather more readily than new grease. Perhaps it is because it is more intimately mixed. It is only fair to remark, however, that a certain degree of skill must be attained in the work before the results are clean and clear. In our tannery (Armstrong Tanning Co.) it has now passed the experimental stage, and the recovery of grease by this method forms a part of the daily routine.

Though this method has been devised particularly for recovering harness tannery waste, no doubt it could be adapted to the recovery of any kind of greasy scrap.

The only apparatus necessary is a large round tank furnished with a steam coil. This tank should be about five feet in diameter and about four and a half feet in depth. (Fig. 1.) The staves should be not less than two inches in thickness, and three is better, in order to keep the contents hot so long as possible after the steam is turned off. The tank should be furnished with a cover, sectional to permit of easy removal. A few planks and a few burlap sacks will answer for this. The steam coil should be brass, and should be mounted on a shelf a few inches above the floor of the tank, so that it will not be clogged by the

debris. It should be pierced with 1/8 inch holes every three or four inches, bored toward the center of the tank, so as to keep the contents in a state of agitation while the steam is turned on. A hole should be bored in the staves near the bottom, and fur-

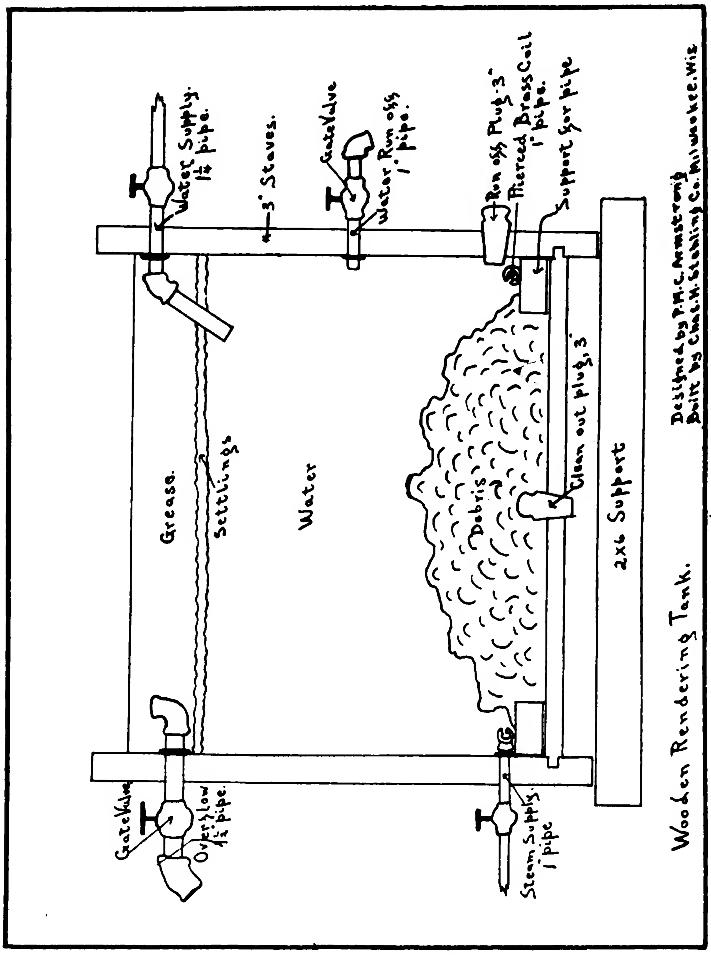

Fig. 1.

nished with a plug to let off the water. It is desirable that a water connection be let into the tank for filling, but if this is not convenient the tank may be filled by means of a hose. Near the top of the tank an over-flow pipe is let into the staves, furnished with a gate valve, for running off the grease, and about

half way down another drain pipe, for regulating the height of the water in the tank. This is for use in event of a threatened boiling over.

The only other necessities are a few tubs for holding the grease, (old oil barrels sawn in two are good), and a dozen or two pressed iron pans for running the grease into moulds.

In general, to recover any sort of greasy scrap the tank is filled a little over half full of water, and brought to a boil. The scrap is then thrown in a little at a time until the whole mass is boiling. It is then treated with the necessary chemicals, the steam is turned off, and the grease is allowed to settle to the

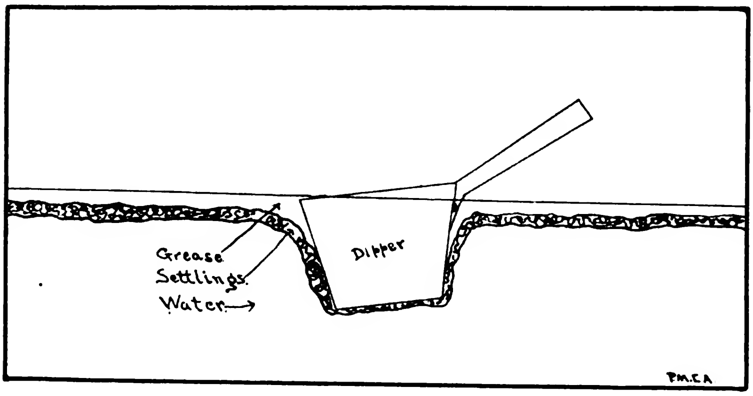

Fig. 2.

top. The longer the grease is allowed to settle, the clearer it will be. If the tank is made of too thin material it will get cold before the grease is settled out. The same is true if the tank is not covered up, especially in cold weather, as the tank makes so much vapor that it must be set up out of doors. When the grease is clear it may be run out of the overflow into the tubs, or if there is not enough to permit of this it may be skimmed off with a dipper, by sinking the dipper almost vertically into the tank, and permitting the grease to flow slowly over the rim. (Fig. 2.)

When the grease becomes hard in the tubs it nearly always is more or less mixed with water, and there is always a coat of settlings on the bottom. It is, therefore, wise to scrape off the settlings, and melt the grease again in a jacket kettle, where it

will settle out perfectly clear, and is then run into the pans. A pan about 20 inches by 14 inches, 4½ inches deep holds about twenty pounds of grease, and is a convenient size. Round milk pans holding about five quarts may be bought in any hardware store, and answer very well, but the cakes do not pile so well as the rectangular ones.

It does not work satisfactorily to mix the scrap, but it is better to save each kind by itself until there is enough for a batch. Each kind of scrap requires a little variation in the treatment, so we shall take them up separately.

Buffings.—Take not more than three barrels of buffings, and add them slowly to the boiling water, stirring them in well. When the whole mass is boiling, pour in a gallon or so of commercial hydrochloric acid (Muriatic Acid). Boil vigorously for about five minutes, or until the buffings all change from brown to light red, and begin to disintegrate. Then turn off the steam, cover the kettle, and settle several hours before running off. The yield should be about twenty-five to thirty pounds of grease from every hundred pounds of buffings, according to the skill of the renderer.

Whitenings.—Whitenings are treated in the same way as buffings, but must not be boiled very hard, as the whitenings disintegrate much more easily than the buffings. Use only about half a gallon of acid. Take three barrels at a time. Whitenings give a very large yield of grease, as there is always a coating of grease on the flesh side of the leather before it is whitened. The yield should never be under forty per cent. of the weight of the whitenings, and frequently goes over fifty.

Trimmings (Unblackened).—Trimmings must be boiled for ten or fifteen minutes before adding the acid, to thoroughly remove the grease. Take only two barrels at a time, and use one gallon of acid. Yield about twenty-five per cent.

Trimmings (Blackened).—In order to destroy the blacking add a gallon of acid to the water just before putting in the trimmings. The grease will appear very black at first, and another gallon of acid is added when the batch has come to a boil. Boil until the foam on the top of the grease turns from black to light brown. This will take ten or fifteen minutes. Settle over night. On account of the heavy boiling the grease becomes somewhat

emulsified with the water, and settles out very slowly, so that it frequently is found, on skimming off the grease, that there is a large quantity of emulsion still unsettled, under the grease. When this is the case, first skim off what grease has already settled off, and then boil it up again. When the grease has been boiled too long the first time it sometimes has to be boiled over several times before all the grease is settled out. Yield about twenty per cent.

"Black Grease."—By "black grease" we refer to the grease which has been slicked from the blackened leather. It is the grease which has been used to "set" the blacking, and is full of blacking itself, so that it is very difficult to dispose of it. Most degreasers will not buy it at all, and it is usually burned. It is quite possible to recover it by the water method, however, if proper care be taken. The recovery of this grease has been the subject of a long series of experiments on the part of the writer, and this valuable material is now saved in our plant. The blacking in the grease is a fine precipitate of mixed ferrous and ferric haematates. These compounds were found to be destroyed easily by oxidizing agents such as Chromic Anhydride, Potassium Permanganate, Hydrogen Peroxide, and even by Nitric Acid. Other acids also removed the color, as iron haematates act as indicators, but the color returned on the addition of alkalis. But when an oxidizing agent was used, the color could not be restored, even by the use of a reducing agent, proving that the haematate had completely lost its character. In practice, however, it was found difficult to oxidize the blacking, as each particle of the precipitate was surrounded by a protective coating of grease, which prevented the oxidizing agent from coming into contact with it. In order to give the oxidizing agent a chance to work is was necessary to get the grease into a very fine state of division, and this was accomplished by boiling it with a small quantity of Sodium Hydroxide, which saponified a portion of the grease, and the soap so formed in turn emulsified the rest. In this state no difficulty was found in bleaching it, and the grease was released from the emulsion simply by adding an excess of hydrochloric acid. This, of course, resulted in the formation of some free fatty acid, but as many harness leather tanners already use a good quantity of stearic acid in their stuff-

ing, sold to them under trade names, it would be of little consequence, and makes the grease appreciably harder, which is a decided advantage, as it would otherwise be rather soft. To obtain good results in practice requires some skill, but the high percentage of grease recovered well repays experiment. A skilled renderer can recover seventy-five to eighty per cent. of the weight of the crude grease, and as it is worth at least six cents a pound as stuffing when bleached it can readily be seen that a great saving is effected.

To recover this material use only one barrel of "black grease" at a time. Fill the tank about half full of water, and add two pounds of commercial sodium hydroxide (Caustic Soda) (Soda Lye). Bring to a boil. Then add the black grease rapidly, and boil until the grease is all emulsified, and appears to be dissolved in the water, which will turn coal black. This will not take over two or three minutes. Then add a half pound of commercial Potassium Permanganate or Sodium Permanganate, and boil five minutes. After stopping the boiling add very slowly one and a half gallons of Muriatic Acid. As there is always some carbonate present in the caustic soda, there will be an effervescence due to the released carbon dioxide, so that care must be taken or the grease will boil over. When the foaming has ceased, boil again, cautiously at first, and later vigorously. About five minutes should be sufficient, but the exact point to stop can be ascertained only by experiment. If it is not boiled long enough only a part of the grease will be recovered, and if too long it will be very difficult to settle it out. This grease cannot be run out of the overflow, but must be skimmed off with a dipper. (Fig. 2.) It should always be settled again in the jacket kettle, as it is invariably full of brown matter (Manganese Dioxide), which is easily removed by settling. This may be avoided by using oxalic acid in place of hydrochloric acid, but the expense is considerably greater, and a part of the oxalic acid remains in the grease to the injury of the leather. It is more satisfactory to settle it out in the jacket kettle. This grease is too soft to use alone, but may be used in the stuffing in place of tallow. Its hardness is about that of cake tallow, or a little harder.

Table Grease (From the Setting Table).—As this grease is usually pretty clear, it is unnecessary to use any acid, nor should

it be boiled. Make the water just hot enough to melt the grease rapidly, and permit it to settle. Nearly all of the grease should be recovered.

Floor Scrapings.—This is usually good grease mixed only with dirt which is on the floor, and may be recovered by settling alone, but a little acid facilitates matters. Melt the grease in the boiling water, and add about half a gallon of Muriatic Acid. Boil very gently, so as not to emulsify the grease, for one minute, and allow to settle.

Other Scrap.—Any other scrap containing grease or oil may be extracted by the methods above described, by varying the process slightly. The only things to be observed are not to use too much acid, and not to boil too long, otherwise the grease settles out with great difficulty. Sulphuric Acid should not be used, as it is not volatile, and, consequently, not removed by boiling, so that it tends to keep the grease emulsified with the water, and it does not settle well. Also, the presence of the sulphuric acid in the grease would be injurious to the leather, as it has a powerful corrosive action.

NOTE ON ANALYSIS OF MOELLON.

BOSTON, MASS., Oct. 9, 1913.

EDITOR JOURNAL AMERICAN LEATHER CHEMISTS ASSOCIATION.

DEAR SIR:—

I note the letter in regard to moellon analysis in the October number of this journal by Mr. J. H. Yocum, and take this opportunity to offer some suggestions in reply to the questions that he asks.

First. Is the chemist's analysis of a moellon other than moisture of value?

It is obvious that the determination of moisture is of value to show the tanner how much water he is buying, and also to regulate the amount of oil contained, when making a fat liquor.

Degras former may have some value. For instance in making an alkaline fat liquor, a high percentage of degras former tends to make a better emulsion. For currying some leather like vegetable tanned patent leather, where the moellon is mixed with

cod oil and rubbed into the leather, a thin moellon with lower percentage of degras former is desirable.

The percentage of free fatty acids is probably of some value, which can best be figured out by a tannery chemist at the tannery.

The percentage of ash is surely of some value, and iodine value, hide fragments, unoxidized oil, etc. are considered of value by some chemists. Next to the amount of water, the percentage of unsaponifiable and its nature may be considered of most value.

Second. Is not the chemist justified in expressing an opinion, when the character of the unsaponifiables and their quantity is such as exists in this case?

We must assume that the unsaponifiable has been determined carefully by saponification with alcoholic caustic potash and extraction with ether. That is not such a difficult matter, but the determination of the character of the unsaponifiables depends largely upon the method used and the ability of the chemist. In Lewkowitsch, Vol. 1., page 478, directions are given for boiling the unsaponifiable with acetic anhydride and determining the nature and amount of the unsaponifiables. In this connection it may be mentioned that the directions in Gill's Handbook of Oil Analysis differ much from those in Lewkowitsch and are probably in error and misleading. The writer has tried out most of the methods for the determination of the nature and amount of the unsaponifiables in moellons, and feels sure that in their present state, they are not very accurate, and much is left to the chemist's opinion. However there is nothing to prevent him using his opinion.

Third. Does not the above analysis justify the opinion of the chemist in stating that, in his opinion, a moellon under these conditions contains wool grease?

Assuming that the moellon in question contained 2.92 per cent. unsaponifiable and these were found by test not to contain mineral oil, the unsaponifiable might contain traces only of cholesterol, and the bulk of the unsaponifiable may be neither cholesterol, nor mineral oil. Some whale oils that are used in making chamois contain nearly 10 per cent. unsaponifiable, which is not cholesterol, or mineral oil.

All moellons, even the purest pressings from the chamois

skins, will show the green isocholesterol test when the unsaponifiable is dissolved in acetic anhydride and a drop of sulphuric acid added. The sheep grease squeezed out of the skins, before tanning contains considerable cholesterol and isocholesterol, and it is reasonable to assume that when the skins are tanned in oil, the grease and alcohols are worked out into the moellon. It would seem that the chemists should have an accurate method for determining the amount of cholesterol, and from that figure the wool grease and the maximum amount of cholesterol that would be allowed in a pure moellon, the same way that they allow for a certain amount of glucose in pure unadulterated leather. The writer wishes to state here that, when the cholesterol is in small amount, the chemist cannot say for certain that wool grease has been added to the moellon.

Fourth. Is it necessary to modify such an expression of opinion to homologues of wool grease, when the absence of mineral oils is established?

In the absence of mineral oil, in the unsaponifiable, the chemist cannot be sure of the presence of added wool grease, unless he determines the cholesterol quantitatively, and finds an amount in excess of the average.

In the present state of these methods, it is likely that chemists will differ in their opinions as to whether a sample of moellon does, or does not contain wool grease.

Yours truly,

C. EACHUS.

SALT STAINS ON HIDES.[1]

By L. L. Lloyd, Ph. D.

Hides which are collected in summer or even warm weather are liable to become slightly decomposed; the salesmen in the skin auctions have recourse to salt which is sprinkled on the fleshside of the skin in order to prevent decomposition of the hide, which is to a large extent responsible for damage to the pelt.

Another source of damage may be due to the action of salt upon the skins with the production of so-called "salt stains."

[1] *Collegium*, 1913, pp. 188-93.

The salt that is sprinkled on the skins dissolves in the water of the skin giving a concentrated or strong solution of salt which then reacts with the hide substance. This action has been proved by the following experiments upon hide which was treated with sodium sulphide for the removal of the hair and was then well washed with distilled water. The prepared hide was stretched across small wooden frames and sprayed with solutions of salts, the pieces were then kept in a moist atmosphere in a desiccator. One piece was sprayed with a solution of 1.0 per cent. of mercury chloride to prevent putrefaction and another with the same solution of mercury chloride in which pure salt was dissolved to make a ten per cent. solution. After several weeks the piece that was treated with mercury chloride solution showed little change except that a pale dirty yellow color gradually developed. The piece that had been treated with salt and mercury chloride soon began to change in color and soon developed a yellowish brown tone. The production of the color is due to the decomposition of the hide substance by the neutral salt. The hide substance being amphoteric reacts with the salt to give hide-acid substance and hide-alkali substance which may be represented by the following equation:

$$\text{Hide substance} + NaCl + H_2O \rightarrow \text{hide substance } HCl + \text{hide substance } NaOH.$$

This reaction is confirmed by extraction of the two pieces of treated hide with the same volume of slightly warm water. The piece treated with mercury chloride gave practically no extract. The piece treated with salt and mercury chloride gave an appreciable extract of hide substance.

These experiments were repeated using known quantities of salt and the chlorine in the aqueous extract estimated. Although the results by no means agree, varying beyond 20 per cent., the chlorine found in the extract was always considerably less than the amount added in the form of salt. The material after thoroughly washing with cold water contained considerably more chlorine than untreated hide. From these results it is apparent that hide-alkali substance is more soluble than hide-acid substance. Exactly similar properties are possessed by wool-alkali substance and wool-acid substance.

The reaction of different parts of hide with salt solution varies very much, and this appears to depend upon the rate at which water is absorbed by the hide.

The pale yellowish brown color of the hide that had been treated with salt and mercury chloride was changed to a pale yellow after washing with water.

Similar experiments to the above were made with sodium sulphate and with salt to which magnesium and calcium salts were added.

Sodium sulphate acts more powerfully than salt upon hide substance, the color is similar to that obtained by salt, but after washing a browner tone is obtained with the hide-sulphuric acid substance than with the hide-hydrochloric acid substance.

G. Abt, Comptes Rend., 1912, 155, 220—222, has found that the color of the stains upon salted hides depends upon the salt used. Bad stains are obtained when the salt contains calcium sulphate. The leather was rich in sulphuric acid and the stained portion contained abnormal amounts of phosphoric acid and calcium, the phosphoric acid being no doubt obtained by bacterial decomposition.

The experiments made by the author with salt containing small amounts of impurities of calcium and magnesium salts in presence of mercury chloride gave practically the same results as pure salt. From these results it appeared most probable that the chief cause of damage was bacterial decomposition, the bacterial action being probably aided by the neutral salt reaction. Several experiments were made upon hide with pure salt and with salt containing common impurities along with bacteria. The bacteria were obtained by using a sewage that was practically a household effluent, and this was employed to dissolve the sodium chloride and other salts. For the purpose of comparison some pieces of hide were treated with the solutions to which mercury chloride had been added.

The pieces that were treated with salts and bacteria developed colors far more rapidly than those similarly treated with the salts and mercury chloride.

In the experiments with salt along with small quantities of substances, such as are present in rock salt or poorly refined salt,

the bacteria developed more quickly and gave different colors according to the salts added and also to the nature of the salts.

The colors obtained varied from yellowish brown, dull red, rusty brown, blue, to grey tone, and the colors only faded slightly on washing.

That the action was due mainly to the bacteria was proved by the action of bacteria and salt upon hide in the dark and in sunlight. The experiments in the dark developed a deep color in a few hours; those in sunlight were only slightly darker than those treated with salt solution only.

The hide substance is decomposed more rapidly by bacteria along with salt containing both calcium and magnesium salts than with pure salt and bacteria.

The colored portions or stains are slightly removed by washing with water, and on washing with dilute acid a pale yellowish brown tone is generally obtained. If the pieces of treated hide are tanned by means of tannic acid they are nearly all turned to a dull brown or dull grey color. The dull brown color is probably the combination effect of the colored hide-acid substance along with the pigment produced by bacterial action and to a small degree by the iron tannin lake. This dull brown color is obtained when slight decomposition only of the hide has taken place. The dull grey color is probably caused, in addition to that given above, by the iron which is present in the hide substance being more concentrated in the portion acted upon by salt and bacteria, or is present in a simpler form which is capable of forming a tannin lake.

The hide-alkali substance is more soluble in water than hide-acid substance, and consequently bacteria growing better in an alkaline than in an acid medium will have every opportunity for development with decomposition of hide substance. During the bacterial action some of the nitrogen of the hide may be converted into ammonia, this will react with the hide-acid substance causing hydrolysis etc.. with reproduction of a salt.

The manifold number of reactions that are possible with the hide and bacteria in the presence of neutral salts easily explains the loss of hide substance and the production of stains even before the actual process of leather manufacture begins.

H. Becker, Collegium 1912, 408—418, has shown that stains are of several varieties and that different classes of bacteria attack the hide substance in entirely different manners, some penetrating the hide (liquefying bacteria) and some giving surface effects only. Becker has also found that about 0.25 per cent. of zinc chloride or 0.25 per cent. of artificial mustard oil prevents bacterial decomposition.

The author has not been able to confirm Becker's results with either zinc chloride or artificial mustard oil, the zinc chloride is the more satisfactory but some bacteria are still capable of liquefying hide, if the material is thoroughly plumped before treating with the zinc chloride.

The action of salt in presence of mercury chloride, to prevent bacterial decomposition, upon hide substance gives a yellowish brown coloration to the hide. This action was allowed to take place during three months, the hide was then well washed with water and tanned. Before tanning the marks were distinctly seen on the grain side, although only the flesh side had been sprayed with the salt mercury chloride solution. The marking on the flesh side, after tanning, was slightly darker where the hide had been treated with salt than the untreated portion of the hide, but the hide was quite free from stain effect on the grain side. The leather so produced was degreased by alcohol and benzene, after drying, the stain or marking effects upon the flesh side were still slightly darker than the untreated portions. The grain side presented practically an even appearance, but when held up to the light showed a slight dull brown stain effect.

Similar experiments to the above were made upon the grain side of the hide.

The action of the salt upon the grain side produces far darker colored stains or markings than upon the flesh side. The color is a rustier brown than that obtained on the flesh side and gives a decided green grey tone on tanning, the color remaining even after degreasing.

H. Becker (loc cit.) has shown that colored effects are produced by different bacteria, and that those bacteria that develop on the surface produce a pigment which is removed by washing.

These surface growths I have found to have little deleterious effect on the leather finally produced.

The action of bacteria and salt upon the grain side gives many colored stains or markings which are not so completely removed, as similar ones on the flesh side, by washing with dilute acid. These stains are probably more permanent than those obtained on the flesh side by the iron which is present in the pigment cells combining with the colored substances produced by bacterial action to form colored lakes.

From these experiments it would appear advantageous to spray skins with a solution of mercury chloride or of mercury chloride and salt immediately on arrival at the skin auction. The combined action of the salt and mercury chloride is probably the more suitable on account of the less toughening action than when mercury chloride alone is used. This could be recommended if the skins were washed immediately after flaying to remove blood, etc., and then treated before any decomposition had taken place. If, however, the hide is already partly decomposed, the decomposition due to the salt reaction is increased, and the mercury chloride is also decomposed such that bacterial decomposition is not prevented. This reaction was observed when the hide was sprayed with a 0.1 per cent. solution of mercury chloride.

J. H. Yocum, J. Amer. Leather Chem. Assoc. 1913, 8, 22—28, states that skins salted in winter months with clear salt solution seldom have stains, but in summer months with clear salt water stains are frequent. Yocum mentions that in the States and Canada the salt is not denatured and there is no tendency to under-salt the skins, the stains are due, according to Yocum, to hæmoglobin and salt owing to the blood not being properly washed out from the skin, or to too high a temperature during curing.

It appears more probable that the blood would aid the development of bacteria and that the stains or spots are produced by bacterial decomposition along with the neutral salt reaction.

This view is moreover upheld by the following experiments. Pieces of hide were treated with salt solution and spotted with blood, and, instead of using mercury chloride as disinfectant, some of the pieces were sprayed with an emulsion of high boiling

point cresol and soap. The pieces were kept for several weeks and then well washed with water. Where the hide had been treated with blood and salt, the color was slightly darker than the portion treated with salt alone, but after tanning the pieces could not be distinguished from one another.

This is as one would expect because the skin already contains sufficient iron to produce a stain, the added iron in the form of blood being negligible.

The pieces that were not treated with the disinfectant began to decompose more quickly on the blood stained portions, the action being bacterial.

The action of salt or neutral salts upon hide increases with increased plumpness or possibly hydration of the hide.

A far more important factor commercially is that salt reacts much more readily upon hide substance that has already commenced to decompose. The putrefaction of the hide is accompanied by liquefaction of the hide substance, and possibly some organic acids are produced during the decomposition. The presence of organic acids along with soluble mineral salts and water leads to the production of mineral acids which combine with the hide substance with formation of a less soluble hide-acid substance.

The increased action of salts upon hide already partially decomposed has probably led most chemists to believe that the stains "Salt-stains" have been produced solely by the action of the salt upon the hide, especially when it has been shown by several investigators that impure salt gives stains more readily than pure salt. The presence of traces of other salts in sodium chloride also aids in the development of bacteria when such salt is added to a medium upon which bacteria develop.

The salted skins are treated by the Fellmonger with lime, and sodium sulphide, or with sodium sulphide. When lime alone is used it is necessary to completely remove the salt before the skin is treated. This is done by soaking in clean cold water. The washing will remove the salt, and, as stated above, some of the hide-alkali substance, leaving the hide-acid substance. Although the lime is only applied to the flesh side of the skin and the skin then washed before pulling, some lime will come into contact

with the grain side of the skin that has been acted upon by salt, which will react with the hide-acid substance, left after washing, with formation of a calcium salt and a hide-hydrate. This hide hydrate will most probably be more easily decomposed by bacteria than the hide substance that has not reacted with neutral salts. The flesh side, which has been mainly treated with salt, will therefore give a large amount of soluble hide substance. This is, however, most important with the grain side, where although salting has not been done the reaction with the strong salt solution formed is practically unavoidable.

The skins after leaving the Fellmonger are limed for the removal of hairs, etc., in which process bacterial action is most important. The bacteria will naturally develop most readily where partial decomposition of the hide has already taken place; the bacterial action being aided in these portions by the salts produced from the lime and the hide-acid substance.

The Fellmonger, during winter often places the skins, after liming, etc., in stoves in order to assist in the pulling of the wool. The warming, similar to the heat of summer, no doubt helps in the production of stains by aiding bacterial action.

When sodium sulphide is used greyish stains are more frequent in summer than in winter. These stains appear to be caused by iron sulphide. The iron in the pigment-cells having been liberated by bacterial, or neutral salt reaction, which then reacts with the sodium sulphide.

If salt is left on a skin, and this comes into contact with lime or lime water, there is a secondary reaction that should increase the gelatinization and consequently loss of hide substance. This is, however, not found to be the case.

Some pieces of hide were treated with salt solution, well washed with water, and then treated with lime water; others were treated with salt solution and without washing were treated with lime water. A third portion was treated with lime only.

In the first case the skin plumped fairly well and was accompanied by the development of a slight yellow coloration.

In the second the skin did not plump well and was not so clear as those that had been well washed.

In the third case the skin plumped up well and quickly.

At first sight these experiments do not appear to give results that one would expect. In the first case hide-acid substance would be present in the skin which on treatment with lime would give hide substance and a calcium salt, from which one would not expect the plumping to be retarded.

In the second case the plumping should be more rapid because the salt will react with the lime giving caustic soda and calcium chloride. The reaction between the two being aided by the presence of an amphoteric substance—skin—which absorbs the alkali. The caustic soda should theoretically cause a more rapid gelatinization of the hide than lime.

Organic salts do not react with amphoteric substances like gelatin, silk, etc., so readily as inorganic salts, because the organic acids are more easily removed by solvents. This applies especially to skin, and also to gelatin rendered almost insoluble in water by means of formaldehyde. The skin, however, contains some fatty and also some organic acid substances, and these act upon the caustic soda as it is produced leaving the inorganic acid combined with the hide which prevents the plumping.

The stains that are most prominent are those that are obtained by the action of aerobic bacteria, the hide being liquefied from the flesh side through towards the grain side. The same bacteria naturally act very detrimentally upon the hide when they develop upon the grain side.

From the consideration of these results it appears necessary to find some cheap substitute for salt to prevent the putrefaction of the skins, and also to prevent decomposition of the skin by the neutral salt reaction, before reaching the Fellmonger, Mercury chloride, although preventing bacterial decomposition, makes the hide tough, and moreover the mercury is not easily removed from the hide. Again when putrefaction has already set in the decomposed hide substance reacts with the mercury giving mercury sulphide, etc., which gives a stain extremely difficult to move so that the leather produced could only be used when dyed dark shades.

In place of the salt-mercury chloride of Yocum, or of the methods proposed by A. Seymour-Jones in which formic acid or the formic-mercury process are used, it appears to the author

that some organic antiseptic or an organo-arsenic compound would be most efficient for protecting the skins from decomposition. The experiments with emulsions of organic compounds along with soaps appear to be leading to fair results.

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ABSTRACTS.

What Possibilities are Suggested by the Production of Artificial Tannin? L. POLLAK. *Collegium*, 1913, 482-4. Not only have artificial dyes added a vast number of new shades, and cheapened the dyeing process, but they have made possible a much more exact knowledge of the relation between the chemical constitution of dyes and their effect on fabrics. Dr. Pollak suggests that a similar development of knowledge of the chemistry of the tanning process may result from the discovery and study of tanning agents whose constitution is known. We may, for example, be able to study the influence on tannage of one or more methyl groups, acid groups or hydroxyl groups, which in default of an oriented formula for natural tannins has not heretofore been possible. We may be able to determine exactly what effect non-tans have on tannage, and so clear up some of the darkest regions of leather chemistry. In a practical way, it may be possible that natural and artificial tannins will mutually supplement each other, so that for instance a leather like oak may be made by adding artificial tans to mangrove. Any considerable development along the lines foreshadowed by Stiasny must raise the price of phenol. Dr. Pollak hopes that with more exact knowledge of the constitution of the natural tannins they may themselves become the raw materials for the production of artificial tannins of greater purity and value. L. B.

The Role Played by Bacteria in the Production of Salt-Stains on Hides and Skins. G. ABT. *Collegium*, 1913, 204-6. Dr. Abt has isolated from a salt stain a bacterium which forms on gelatin dark brown or black colonies. A gelatinous precipitate of calcium phosphate seems to have the power to collect the coloring matter and so intensify the color. L. B.

Estimation of Acid in Handler Liquors. F. TANZER. *Collegium*, 1913, 194-7. The various methods which have been proposed are briefly reviewed. Two things are necessary; a suitable indicator and a precipitant for tannin which shall not change the acid content, but precipitate all the tannin. Pine bark liquors change their brown color to a clear green at the instant when neutralization is complete. Thus when liquors are made from pine alone, no other indicator is required. If a liquor containing no pine is to be titrated, a definite quantity of pine-bark liquor of known acidity is added, to serve as indicator, and a correction made in the reading to allow for the alkali used by the added pine liquor. If the other liquor has a strong color so as to mask the color-change of the pine,

the method must be varied, as stated below. For a pure pine liquor, take 25 cc., dilute to 750 cc. in a porcelain vessel with water at 40° C. Titrate with N/5 NaOH till the green color appears. To a liquor whose acidity had been thus determined acetic acid was added and another titration made. The increased acidity was correctly estimated by the same method. When the color of the liquor to be examined is so intense as to mask the color-change of the pine bark liquor, the tannin and other coloring matter are precipitated by means of alcutin, and the pine liquor added to the clear filtrate, which is then titrated in the manner above described. It is necessary to apply a second correction because of the acidity of the alcutin solution. L. B.

The Phlobaphene-dissolving Property of Neradol D. G. GRASSER. *Collegium*, 1913, 478-81. The author analyzed a number of mixtures of solid ordinary quebracho (66.0 per cent. tannin) with neradol D (32.5 per cent. "tannin"), sulphite-cellulose extract (22.6 per cent. "tannin") and a mixed liquor having 3 per cent. tannin.

Mixture number.	Grams solid quebracho extract.	Grams mixed liquor.	Grams sulphite cellulose extract.	Grams Neradol D.	Tannin in mixtures Per cent. calc.	Tannin in mixtures Per cent. found	Absolute gain, per cent. tannin.	Gain of tannin calculated on tannin of quebracho and liquor.
1	90	—	—	10	62.7	64.7	2	2.2
2	80	—	—	20	56.1	58.7	2.6	3.3
3	60	—	—	40	52.6	56.9	4.3	7.1
4	50	—	—	50	49.3	55.2	5.9	11.8
5	30	—	—	70	42.6	47.3	4.7	15.6
6	20	—	—	80	39.2	42.3	3.1	15.5
7	20	60	20	—	17.5	16.1	—1.4	—9.3
8	10	30	10	50	26.0	27.3	1.3	17.3
9	5	90	5	—	7.1	4.9	—2.2	—3.7
10	5	80	5	10	20.3	20.9	0.6	10.5

It is thus shown that neradol D carries the phlobaphenes of quebracho into solution, and overcomes the apparent tannin-destroying property of sulphite-cellulose. A used liquor of 92° barkometer, having 18.0 per cent. tannin and 4.0 per cent. non-tans, on being strengthened to 132° with neradol D showed 28.5 per cent. tannin and 2.0 per cent. non-tans. For tannage of upper leather, the hides may be placed for 24 hours in a neradol D liquor of 3° barkometer, and then tanned in 4 days in a series of 4 vats, whose liquors are made up from a spent liquor ot 10° bk. made up with a 50:50 mixture of quebracho and neradol D to 12°, 19°, 26° and 30° respectively. The use of neradol is justified by its solvent action on the reds in the liquor, by the saving in time and by the color and toughness of the leather. Leather tanned with neradol D alone was tanned in

3 days, had a yellowish white color, was very tough, and gave the following analysis (unstuffed): water, 15.53 per cent.; ash, 0.93 per cent.; fat, 1.26 per cent.; water-soluble, 0.0 per cent.; hide-substance, 45.36 per cent.; combined tannin, 36.92 per cent.; specific gravity 0.642; tannage number 81.4; rendement number 220. The leather has a greater capacity for fat than ordinary leather. G. thinks neradol D may be classed with the best vegetable tanning materials. L. B.

Neradol Tanning-material. W. MOELLER. *Collegium,* 1913, 487-95. Tanners agree that néradol might be used to advantage in a variety of ways, but for its high price. The author disputes the claim of the makers that neradol shows close resemblance to the natural tannins. The iron reactions of neradol are rather analogous to those of other phenolic bodies than to those of tannin. Neradol gives blue only with ferric chloride, not with other iron compounds. The neradol-gelatin precipitate is almost entirely soluble in excess of strong neradol solution. On diluting the solution an amorphous precipitate is thrown down. Analysis by the Löwenthal method gives 33.6 per cent. water, tannin 7.2 per cent., non-tans 59.2 per cent., results more like sulphite-cellulose than a vegetable tanning extract. By the hide-powder method the same sample gave 33.4 per cent. tannin. Neradol differs widely in character from vegetable tannins, being nearer to aldehydes and phenols, with which it shares its ability to tan. The author therefore objects to calling it a synthetic tannin. Of the material absorbed by hide, 1.5 per cent. of the 33.4 per cent. is ash. The water-resistance (Fahrion) of neradol leather is low. Pieces of calfskin treated for 24 hours in strong solutions of neradol (up to 34° Bé.) gave harsh leather. On extending the treatment to 12 days partial solution of the skin took place. The author attributes the bleaching action of neradol on bark leather to its solvent action on tannin dissolving tannin out of the surface. L. B.

Neradol Tanning Material. E. STIASNY. *Collegium,* 1913, 528-31. Dr. Stiasny comments on the observations of Dr. Moeller (preceding abstract) in regard to neradol. First as to the bad results. Dr. Moeller treated pieces of hide with liquors ranging up to 34° Bé. and says he obtained brittle leather and other bad results. The directions furnished by the makers recommend liquors from 0.5° to 2° Bé. Sodium sulphide in weak solutions is a good unhairing agent. In strong solution or too long treatment, hide is destroyed. Bates must be used correctly or they do damage. Even a vegetable tanning extract will not make good leather at 15° Bé. Used properly, neradol D makes tough leather. It is not recommended for use alone in the making of heavy leathers. The fear that the use of neradol D will give a high ash content to the leather is groundless. Neradol leather has an ash of less than 1 per cent. Dr. Moeller asserts that neradol gives blue-black color with ferric chloride, but not with other iron solutions, and refers this reaction to unaltered phenol groups. On the contrary, neradol D reacts with all iron solutions,

and a piece of neradol leather placed in such a solution is colored an intense blue. The difference in behavior between neradol and the tannins with respect to gelatin solution is due to the acidity of neradol. An equally acid tannin solution behaves in a manner quite similar to neradol.

L. B.

Rendering Tanning Extracts Soluble with Sugar and Sodium Bisulphite. E. O. SOMMERHOFF. *Collegium,* 1913, 484-7. Solid quebracho extract moderately heated with a concentrated solution of cane sugar becomes much more easily soluble. Such a sugar and quebracho extract is not suitable for drum-tannage because by its swelling effect on the hide it hinders the penetration of the tannin. In fore-tannage, where a pronounced swelling is desired, a dilute quebracho solution containing sugar may be used. The author's cell-colloid theory explains the action of sugar in the same manner as that of acids. All animal and vegetable tissues absorb and hold acids. It is not improbable that the acid combines with albumin much as water does. From the point of view of the cell-colloid theory the acid diffuses through the cell-wall of the minute colloid cell, replacing one or more molecules of the water of the cell-content, not attacking the cell wall. This infinitely thin membrane is stretched by the increased cell-content and thus gives to the entire tissue a stiff swollen character. Silk-dyers speak of the "enlivening" effect of acids. The action of alkalies is similar to that of the acids, but in addition they attack the cell-wall, soon closing its pores and reducing the albumin mass to the condition of a gelatinous solution. Sugar behaves in an intermediate manner between acids and alkalies. Sugar is not, however, used in practice to render quebracho soluble. In tannage with basic mineral salts, to prevent too rapid formation of colloid precipitates, or in other words to facilitate the diffusion process in the hide, a salt which diffuses easily and not a swelling electrolyte is added, *e. g.,* common salt. In the quebracho solution the place of salt is taken by sodium bisulphite, pointing a strong analogy between mineral and rapid vegetable tannage. It is not unlikely that in the old bark tannage in which the solutions were dilute the electrolyte role was taken by calcium and magnesium salts present in the water. The sodium bisulphite in the quebracho solution, besides its use as an electrolyte, has a special chemical function as a sulphite. A part of this function is to prevent by means of its reducing action the too rapid oxidation of the quebracho extract. There is also a more fundamental reaction between the bisulphite and the quebracho. The quebracho solution may be able to reduce some bisulphite to colloidal sulphur. The author has in a previous paper suggested that the tanning action of sulphite-cellulose extracts may be due at least in part to colloid sulphur. The author agitated finely divided sulphur in hot quebracho solution, and found that it increased the solubility of the quebracho. On long boiling the solution smelled of SO_2, and on standing in the cold of H_2S. Some reaction must have taken place between the sulphur and the quebracho. Whether it would ultimately be combined with the tannin as a sulpho-

acid can only be surmised. The favorable effect on quebracho of direct addition of sulphur is no doubt partly due to the fact that sulphur tanned hide has a greater affinity for tannin than the unaltered hides.

L. B.

Research on the Tannin Content of the Waste Liquors from Sulphite-Cellulose Factories. A. STUTZER. *Collegium*, 1913, 471-3. When the liquors have been evaporated to 30° Bé, about half of the solids are capable of combining with hide-powder. The extract contains much lime, combined with acids grouped under the name "sulpholigneous acid," which detracts from the value of the leather. A good method of removing the lime is to treat the liquor with ammonium sulphate, which forms calcium sulphate which is filtered off while the ammonia unites with the sulpho-acids to form easily soluble compounds. Results of such treatment are shown in the table, (percentages in 30° Bé. extract, additions per liter of original liquors:)

	Lime Per cent.	Ash Per cent.
1 Waste liquor without addition	3.24	6.54
2 Ammonium sulphate added, 10 g. per liter	1.67	4.51
3 Ammonium sulphate added, 20 g. per liter	0.28	1.30
4 Ammonium sulphate added, 30 g. per liter	0.08	0.84

The quantity of pseudo-tannin may be varied by the addition of certain substances. The percentages of tanning substance in 30° Bé. extract with additions per liter of original liquor (7° Bé.) as indicated, were as follows: No addition, 49.6; 30 g. ammonia sulphate, 49.6; 30 g. soda, 39.3; 30 g. am. sulph. and 5 cc. 25 per cent. HCl, 45.0; 100 g. glycerin, 38.9; 40 g. soda and 30 g. alum, 50.5; 75 g. sulphate of soda, 51.7; 30 g. sulphate of soda, 52.5; 30 g. magnesium sulphate, 53.4; 30 g. manganese sulphate, 55.8; 30 g. iron sulphate, 57.1; 30 g. zinc sulphate, 57.4; 10 g. bisulphate of soda, 57.2; 20 g. bisulphate of soda, 54.5; 30 g. chrome alum, 63.6; 30 g. ammonium sulphate and 50 g. of 25 per cent. phosphoric acid, 66.6; 30 g. ammonium sulphate and 100 g. of 80 per cent. acetic acid, 51.1; 30 g. ammonium sulphate and then with the following quantities of 74 per cent. lactic acid, 25 g., 58.6; 50 g., 62.9; 75 g., 65.5; 100 g., 64.4. Leather tanned with the extract to which lactic acid had been added was of good color and texture. Addition of salts of lactic acid had no effect in raising the content of pseudo-tannin. L. B.

Agnolina. ANON. *Conceria*, **21**, 171. "Agnolina" is a product derived from wool grease and is composed almost exclusively of cholesterol esters which melt at a low temp. and are not saponifiable by alkalies. This product does not become rancid and easily penetrates the pores of skins, rendering the latter soft and smooth. H. S. PAINE.

Brilliant Finish for Leather. ANON. *Conceria*, **21**, 171. A patent obtained in Germany by the Belvril Co. Limited proposes applying several

coats of a mixture of nitrocellulose and nitrolinolein or nitroricinolein as a means of giving a brilliant and pleasing finish to leather; the solvent should then be allowed to evaporate thoroughly. H. S. PAINE.

Washing of Sheepskins. ANON. *Conceria*, **21**, 265. A patent obtained by Jules Varasses proposed washing sheepskins in a solution of sodium, potassium or ammonium monosulphide instead of with soap.
H. S. PAINE.

Method of Rendering Leather Impermeable. S. L. R. *Gerber Courier*, Oct. 17, 1912, p. 25; through *Conceria*, **21**, 266. Chrome leather which has not been heavily loaded with fat liquor may be made impermeable by applying gelatin which has been rendered insoluble with formaldehyde. The solution of gelatin treated with formaldehyde may be applied directly to the leather or the latter may first be smeared with the gelatin solution and then treated with formaldehyde. H. S. PAINE.

Tanning by the Pujol System. ANON. *Conceria*, **21**, 172. This process consists in tanning the hides in a trench with a double bottom composed of strips of wood 3 cm. thick by 10 cm. wide. The trench is filled with alternate layers of hides and tan and the tan liquor is allowed to percolate slowly through the mass, extracting tannin and transferring it to the hides; a pipe at the bottom carries off the liquor. H. S. PAINE.

Metallic Leather. ANON. *Conceria*, **21**, 171. Skins or leather tanned by any process whatever may be given a metallic coating by the following process. The material, which should be quite dry with pores well opened, is impregnated with silver nitrate by immersing in a solution of the latter. After drying, the leather is placed in closed vessels and exposed to the fumes of phosphorus in carbon bisulfide. The salt is reduced and metallic silver deposited on all the fibers of the leather, thus rendering the latter a good conductor of electricity. The leather may then be coated as desired by placing in an electrolytic silver or gilding bath, etc. H. S. PAINE.

Unhairing and Liming. W. EITNER. *Gerber*, 1913 [39], 225-7, 239-41, 253-5. This article presents an exhaustive resumé of this important subject and a discussion of some of the special problems of present interest. Formerly liming was regarded as first of all an operation for dehairing and such effects as might not reveal themselves until after tannage or finishing of the leather received secondary consideration. In recent times a strict differentiation between unhairing and liming has grown up and the latter subject is receiving increased attention. Although doubtless chemical reaction is important in this process, the author is of the opinion that its theory should be largely based upon a physiological and histological foundation. Before the outer skin of the hide together with the hair can be removed, the mucous layer uniting it with the leather hide proper, must be loosened either by chemical treatment

or by the action of bacteria. For all leathers except sole leather, the mere removal of the outer skin is not sufficient. Besides loosening the hair, it is important to secure loosening of the hide fiber itself. This applies to all soft and flexible leathers. To obtain this result, chemical action is combined with physiological action (bacteria).

For loosening hair both methods are used but the physiological method the least. It is represented by the old sweating process which involves the solution of the mucous layer by the action of bacteria flourishing under favorable conditions; a form of putrefaction of the protein substance takes place. Hair loosening was also effected by the fermentation following the acid formation in bran bates. In distinction from the sweating process, anaërobic, air-shunning bacteria are here active and are much more energetic in decomposing albumins than the aërobic oxygen consuming bacteria (Bacterium vulgare, B. coll,) of the first process. If sweating be prolonged, the anaerobic bacteria (B. putrificus, B. putilus) also develop and there is danger of the hide fiber itself being attacked. The first action is the fermentation of the dissolved or gelatinous material within the fiber rendering it open. When the acid reaction changes to alkaline real putrefaction ensues and the fiber itself is destroyed. The most important improvement in the sweating process is the provision of ventilation in the sweating room. This favors the action of the aerobic bacteria and prevents the growth of the injurious anaërobes. In earlier times, the opposite result was effected by warming the rooms with smoldering tan bark; this consumed the oxygen and the antiseptic action which was assumed did not prevent putrefaction. The primitive process of sweating hides in piles was also defective in air supply. In the modern ventilation process water or steam is supplied to the ventilated chambers to prevent the drying of the hides by evaporation. These details were observed as long as sweating was employed for sole leathers in Scandinavia and America. At the present time the process is chiefly used in wool pulling. The sweating process is gaining vogue again and in America is carried out in systematic rotation like liming or tanning. Since the solution of the mucous or Malphigian layer proceeds at 1—15° C. and putrefaction first begins above 15°, the regulation of temperature is important. In the ancient process at high temperatures where much ammonia was evolved, this was thought to be active in loosening the hair. In reality, the decomposition products of the bacteria requiring air are acid or neutral, and the more radical decomposition producing ammonia comes from the anaerobes at high temperatures. The modern process conducted at a normal temperature with air access should rather be called a biological process than sweating.

The second method of hair loosening by chemical means was first employed with potash, to which lime was later added and finally displaced it entirely. Finally arsenic and alkaline sulphides were used as auxiliaries. In alkaline hair loosening, the mucous layer dissolves in chemical combinations instead of dissociating as in the quicker biologi-

cal process. Research and practice have proven that bacterial action promoting hair loosening is present to some extent. In the hair loosening process by pasting ("Schwöde") with alkaline sulphides, the solution is purely chemical and bacteria cannot flourish in the strong alkaline medium. They can be found however in the hides which have been soaked after the straight lime "Schwöde" used in white leather manufacture. These limes are used but once and do not contain miscellaneous fermentation products, but principally bacteria of the coccus species. In the ordinary lime it is easy to find the products of both chemical solution and biological decomposition. Not only is the outer skin dissolved but also the leather hide to some extent, which is undesirable in the manufacture of sole leather and maximum rendement leather. An absolute separation between hair loosening and hide retention (together with hide loosening) is not possible but the undesired action may be reduced. In concentrated alkaline sulphide solutions there is no bacterial action. For these 3-10 per cent. of sodium sulphide is used which loosens the hair in 1 to 2 days and produces intense swelling which may be used for filling with extract for thick leather. The swelling may be reduced if desired by the use of polysulphides; 32 parts of flowers of sulphur are dissolved in 100 parts of crystallized sod. sulphide, 200 parts water. This is employed in the pasting process or for the liquors of a lime vat.

Besides loosening the hair it is also desirable to loosen the hide for all soft and flexible leathers. Hide substance is like a fabric made up of threads and these composed of still smaller fibrils. If the coarse fibers are tanned as such, firm stiff leathers(sole leather) results. If the intercellular substance be partially dissolved away, according to the extent of this a soft leather is produced. As this substance enveloping the fibers is very similar to that removed in hair loosening, its solution may be effected by the same biological or chemical agents. That hide may be loosened by purely physiological action is illustrated by a form of sweating at one time used in England. The hides were suspended in a thin mixture of powdered charcoal and water until the hair was loose. Not only could sole leather be thus prepared but by prolonging the action soft leather was obtained. Hide loosening is almost exclusively carried out in liming and takes place after the hair loosening. The share taken by bacterial action in the change increases with the age of the liquors and the accumulation of dissolved substance from the hide. In fresh limes the hides become swollen and stiff due to the alkaline action while in old limes the hair is rapidly loosened and soft thin hides result from the preponderating physiological action. The nature of the hide material must be taken account of in liming. The leather hide may be considered as made up of gelatine substance which constitutes the fiber and the surrounding plasma or protein. This last yields easiest to alkaline treatment as is illustrated in glue manufacture where the useless plasma is extracted from the glue leather with lime. The ratio between gelatine

and plasma varies with the animal and individual, the hard goat skin (excess of gelatine) and the soft sheepskin representing the two extremes. The change in hide substance on drying and lengthy storage affects both components and they become less permeable to water and less soluble in alkali; further the plasma is less capable of being decomposed by anaërobic (aërobic?) bacteria. The altered hide is still susceptible to decomposition by anaërobes but resists all other bacteria found in limes or bates. This is an important determining element in liming and the succeeding operations. The action of lime is various, dissolving the plasma of the mucous layer, then that of the fiber bundles. Further it causes the glue forming substance to swell through absorption of water and finally it affects the organisms and their products. Since the extent of the liming process is judged by the degree of swelling the question arises whether this determines hide loosening. If there is no loss of hide substance through action of the alkali, there is no loosening which will characterize the leather. The swollen hide however may easily and evenly undergo hide loosening through bacterial action in the bates as illustrated in glove leather manufacture. W. J. K.

The caustic alkalies, potash and soda have a greater swelling power than lime and these were formerly added to the lime liquors in the form of wood-ashes, to sharpen them. The hides would be put first into a mild old lime, in which bacterial action predominated, and from this "unhairing lime" into a fresher lime with stronger alkali, the "swelling lime." Modern practice combines the two. Not so much for the sake of the swelling effect as to hasten the process and save hide-substance, alkaline sulphides, especially those of soda and calcium, are now often added to the limes. The sulphides loosen the hair quickly by dissolving the mucous layer without physiological effects, which are not now desired in the limes, but are postponed to the bates, where they can be more effectively watched. In limes sharpened with sodium sulphide, the swelling is due both to lime and to caustic soda, formed in the liquor by reaction of the lime on the sulphide. Calcium hydrosulphide, the other substance formed, does not plump, but dissolves interfibrillar substance, without attacking the fiber, so that it acts to loosen the hide, as well as the hair. This property also makes calcium sulphide useful for softening hides which have been hardened by over-heating or long storage. Hydrosulphide of calcium may be added direct, or produced in the liquor by adding red arsenic. By dissolving flowers of sulphur in a solution of sodium sulphide, and adding lime, calcium hydrosulphide is produced, but no caustic soda, and such a lime works like one to which arsenic has been added, reducing the hide, rather than plumping it. The use of arsenic checks the otherwise too exuberant growth of bacteria in the liquors, saving hide substance in this way as well as by the shortening of the process. Such limes, rather than those containing caustic soda, are best for chrome goat, the resulting leather having the soft, full "feel" desired. It is important that in the loosening of the hide fibers their fine fibrils

should not be injured, so that the toughness of the leather shall be as great as possible. The simple loosening of the fibrils will not weaken the leather, since the strength of the whole is equal to the combined strength of its parts. But too energetic action of alkalies or of ferments may weaken the leather by attacking the fiber itself. The microscope will show the effect of bacteria in local weakening of the fiber, or of alkalies in thinning the fibers.

It is said that the limes remove the fat from hides by saponifying it. This effect is slight, because the lime soap is a cheesy insoluble substance hard to remove. The author credits the removal of a great part of the fat to micro-organisms which are carried into the limes by the dirty hides. The most suitable and popular liming system has three pits, the older. middle and fresh. Each hide passes through all three, entering by the oldest, and remaining only one or two days in each. The time for bacterial development is thus short, and the effect of bacteria on the hides relatively small. Limes which smell of ammonia are said to be mild in their action. The softness of the leather from such limes is due to the bacteria and not to the ammonia. The condition of a lime may be judged by the condition of the hide in it, and by bacterial examination. The determination of special organic substances due to decomposition is difficult, and does not often give intelligible information about the condition of the liquor. Determination of alkalinity is important, showing when the liquor needs strengthening.

Dr. Röhm has devised a method of unhairing in which the hair-loosening and hide-loosening are both effected by the solvent action of tryptases. (See p. 408, Sept. number of this Journal.) L. B.

Synthesis of Depsides, Lichen Compounds and Tannins. E. Fischer. Congress Report in *Zeit. angew. Chem.*, 1913 (26), 547-8. The results of 5 years research in this field were summarized. Depsides are the first anhydrides of phenol carbonic acid. Some 20 of these were synthesized, including several trisepsides and 2 tetradepsides, (designations for couplings of 3 and 4 carboxyl groups). Several natural depsides occurring in lichens were investigated. Among these lecanoric acid found in archil was synthesized. Gallo-tannins are acyl compounds of glucose with gallic as digallic acid. The synthesis of this entire group begins with that of the galloglykoses.

These researches have shown that glucose like glycerin is capable of fixing acids in plants, an important principle in plant physiology. The employment of synthetic tannins for the manufacture of leather is excluded by the high cost. Since the tannins are important ingredients of food substances in wine, coffee, tea and sweet fruits and there is prospect of synthetic chemistry conquering this field, it may be hoped that the synthesis of tannin will reach technical significance in the future. Concluding the author compares the two methods of research in natural science, the building up of enormous molecules by organic synthesis and in physics the splitting up in the electrons. W. J. K.

Tannin. M. NIERENSTEIN. Abstr. *Chem. Ztg.,* Vol. 37, p. 1237. The author cannot accept the view of Fischer (preceding abstr.) in regard to the constitution of tannin. Examination of the tannin of hemlock, knoppern and guarana (algarobilla?) has shown that these contain no sugar, thus disproving Fischer's assumption of a glucoside nature for all tannins. Tannin contains sugar in varying quantities, but only about half as much as Fischer's formula calls for. We must have a much fuller insight into the molecule of tannins and tanning materials before the story of the story can be told of the discovery of their constitution and their synthesis.

L. B.

Report on the Employment of Viscosimeters. M. BAHEUX. *Les matieres grasses.* 1913 [6], 3231-4. Engler's apparatus is decidedly preferred to Barbey's ixometer for laboratories which have daily tests to make. For measuring the fluidity at temperatures of 35-40 degrees, Barbey's instrument gives concordant results and several determinations can be made in rapid succession. For the temperature of 100 degrees used in testing thick cylinder oils, Barbey's apparatus requires much more time than Engler's. The temperature of the oil does not correspond to that of the bath and with an oil bath for higher temperatures it is still more uncertain. Another defect is the long tube with two rectangular bends through which the oil must pass. (In the Engler apparatus this distance is insignificant). The coefficient of friction which is independent of the fluidity thus has varying effects on the results. Tests with various mixtures are quoted showing that oils of the same viscosity test by the Engler apparatus often gave different fluidities in the Barbey apparatus and vice versa.

W. J. K.

PATENTS.

Tanning Drum. English Patent No. 12,867. HERRENSCHMIDT & Co., Strassburg.

Phenol-formaldehyde Condensation Products. English Patent 13,431. F. POLLAK, Berlin.

Hide-working Machine. U. S. Patent No. 1,075,887. R. F. WHITNEY, Winchester, Mass.

Leather-staking Machine. U. S. Patent No. 1,074,348. P. BOHACEK, Frankfurt a. M., Germany; assignor to Moenus Maschinenfabrik.

Process for Drying Hides. U. S. Patent No. 1,075,319. W. H. ALLEN, Detroit, Mich. The skin is stretched on a flat plate and a current of air flows from the middle toward the edges.

Method of Treating Rawhide. U. S. Patent No. 1,074,360. A. H. HENDERSON, Baltimore, Md., assignor to Henderson Rubber Co. Ground rawhide is kneaded with water, salt and oil and vulcanized.

Leather-Splitting Machine. U. S. Patent No. 1,075,792. W. D. QUIGLEY, Boston, Mass.

Oil Tannage Process. English Patent No. 13,168. S. R. HOLDER, Mitcham, Surrey. An oil-tanned leather is made by chamoising skins with the grain on, the resulting grained leather being suitable for gloves and like articles. The skins, after being unhaired and limed, are steeped in a sour bran drench for a period varying from one or two days, in ordinary weather, to a few minutes in hot weather. They are then pressed, oil-fulled in the usual way, and heaped in tanks in which they are allowed to heat up to a temperature not exceeding 140° F. The excess of oil is expressed and the skins are finished in the ordinary way.

Processes for Treating Hides and Skins. English Patent 13,952. J. BYSTRON, Teschen, Bohemia. In iron tannage, insoluble basic ferric compounds are formed in the skin by oxidizing a ferrous salt by means of a nitrogen oxide, especially nitrogen dioxide. In one process, the acid-free skins are placed in a solution of a ferrous salt, with the optional addition of neutral alkali salts, and the liquor is oxidized by passing through it nitrogen dioxide, by decomposing nitrites, or by passing into it a mixture of nitric oxide and nitrogen dioxide. Liquefied gas may be used for the supply. By working in closed vessels a given quantity of nitric oxide may be employed cyclically to oxidize the ferrous salt with oxygen taken from the air outside the vessels, or the regeneration may be effected within the vessel itself by passing air through the liquor. The nitrogen oxides may be generated in the vessel by mixing a nitrate with the iron protoxide salt and adding a sufficiency of a suitable acid to liberate nitrous acid. Alternatively, the ferrous solution may be separately oxidized before the skins are immersed, or the skins may be placed in an iron protoxide solution from which their contained alkali precipitates an insoluble protoxide, which is then converted into a basic insoluble compound by nitrogen oxides.

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LLOYD BALDERSTON . . . . Associate Editor

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CHANGES OF ADDRESS.

George W. Priest, to 78 Beech St., East Orange, N. J.

Elting C. Stillwell, to % Anderson Chemical Co., Passaic, N. J.

Frank M. Loveland, to 484 E. Ferry St., Buffalo, N. Y.

C. A. Reisig, to St. James Hotel, Philadelphia, Pa.

Hugh Ross, to Ross-Sellinger Co., Sheboygan, Wis.

John H. Barton, to % Atlas Refining Co., Newark, N. J.

A. L. Dean, to 1844 Yale Station, New Haven, Conn.

W. G. Sprinkel, to 115 S. Main St., Harrisonburg, Va.

W. R Cox, to 911 Winona Ave., Chicago, Ill.

C. B. Kinney, to % Farbwerke-Hoechst Co., 122 Hudson St., New York, N. Y.

TENTH ANNUAL MEETING.

The Tenth Annual Meeting of the American Leather Chemists Association will be held at Atlantic City, New Jersey, Dec. 4, 5 and 6, 1913. The committee having in charge the arrangements for the meeting, has selected the Hotel Traymore as the place of meeting. A suitable room has been reserved for the meetings, and members who desire to retain rooms at the hotel are requested to apply directly to the management. The hotel is run on the American plan, the following being the schedule of prices:

OLD BUILDING

One person, $4 or $5 per day, without bath.
Two persons, $8 or $9 per day, without bath.
One person, $6 per day, with bath.
Two persons, $10 or $11 per day, with bath.

NEW BUILDING

(Each room with separate bath.)
One person, $7 to $13 per day.
Two persons, $12 to $16 per day.

PROGRAM.

THURSDAY MORNING, DECEMBER 4, 1913.

Opening remarks by the President, W. K. Alsop.
Report of the Secretary-Treasurer, H. C. Reed.
Committee Reports.

THURSDAY AFTERNOON, DECEMBER 4, 1913.

Address, "Detection of Mangrove in Admixture with Other Tanning Materials," by George A. Kerr.
Address, "A Comparison of the Extraction of Vegetable Materials Containing Tannin, in Copper and Glass," by L. M. Richeson.
(Prepared by C. R. Oberfell and L. M. Richeson.)
Remarks concerning an Extraction Thimble for use with the Teas' Extractor, by F. H. Small.
Address, by Sigmund Saxe.

FRIDAY MORNING, DECEMBER 5, 1913.

Committee Reports.
Address, "Water and its Purification for Tanning Purposes," by M. F. Corin.
Address, "Quality or Quantity," by J. J. Desmond.

FRIDAY AFTERNOON, DECEMBER 5, 1913.

Address, "Depilating Methods," by Dr. Allen Rogers.

Address, "The Inter-relation between the American Leather Chemists Association and the National Association of Tanners," by Cudworth Beye, Executive Secretary of the National Association of Tanners.

Address, "Further Experiments on the Clarification of Leather Extracts for the Determination of Reducing Sugars," by F. P. Veitch. (Prepared by F. P. Veitch and J. S. Rogers.)

SATURDAY MORNING, DECEMBER 6, 1913.

Address, "Notes on the Determination of Free Sulphuric Acid in Leather," by Dr. Otto Kress.

Address, "Industrial Chemistry and the Leather Industry," by C. R. Oberfell.

Election of Officers.

General Business.

There will be an address by W. H. Dickerson on Sulphite-cellulose Extract.

Papers are also expected from Prof. Henry R. Procter, W. H. Teas and others.

REPORT OF THE COMMITTEE ON "THE QUESTION OF SAMPLING."

The Committee submits the following report to the Association with a firm belief that it has at least accomplished in the main the principal ideas as suggested at the last annual meeting.

The question of sampling has been carefully considered by the Committee with reference to the domestic manufacturer, the importer and the consumer of tanning materials, and it has been the sole aim to propose such changes as will furnish a true representative sample of the material to be sampled.

The principal changes have been made in the sampling of solid extracts, liquid extracts in barrels, and of crude tanning materials. As for the sampling of solid extracts the Committee considered a number of suggestions but were unable to agree

upon any one; so it was finally decided to make two proposals for the consideration of the Association.

It is the desire of the Committee that the Association give the proposed Official Method the careful consideration which it merits.

Proposed Official Methods for Sampling Tanning Materials.

GENERAL:—

Extract whether liquid or solid, and tanning materials in general all contain moisture. The amount of moisture varies with climatic conditions, but especially in liquid, and in most solid extracts becomes less as the extract is exposed to the air. As the value of any material shown by analysis is directly dependent upon the amount of moisture contained, and as an exposure of a comparatively few moments may alter appreciably the amount of moisture it is apparent that the sampling in all its details should be done as quickly as consistent with thoroughness and with great care to expose the material as little as possible to the air. The portions taken as samples should be placed at once in containers as nearly air tight as possible, and preferably of glass. Wood, cardboard, poorly glazed crockery, etc., are all porous and more or less absorbent and not suitable for retaining samples.

Liquid extract cannot be accurately sampled when it contains any frozen material. A sample of extract taken after live steam has been run into the extract has not the same concentration as the original extract. A sample of spent bark which has been standing where dust from fresh ground bark has sifted into it does not represent the degree of extraction of the spent bark. Samples of liquor which have been kept with no preservative in them for some time do not represent the condition of the liquor when sampled.

All extracts and crude tanning materials shall be sampled as nearly as possible at time of weighing, and for every 50,000 pounds, or less, sampled a sample shall be drawn.

(1) SOLID, POWDERED AND PASTY EXTRACTS:

Proposal (A). The number of packages to be sampled out of a given lot shall be ascertained by taking a percentage of the

total number of packages in the lot obtained in the following manner:— Divide the total number of packages by 100, multiply by 0.02 and subtract from 4.

Thus $4,700 \div 100 = 47$

$47 \times 0.02 = 0.94$

$4 - 0.94 = 3.06$ per cent.

$4,700 \times 0.0306 = 144$ Packages.

Provided that for lots of 200 packages and under 5 per cent. of the number of packages shall be sampled, and for lots of 10,000 packages and over 2 per cent. of the number of packages shall be sampled.

Proposal (B). For every shipment of extract to be sampled the number of packages shall be 14 for every 50,000 pounds, or less, except for lots of 200 packages and under 5 per cent. of the number of packages shall be sampled.

NOTE:—The proposal which is adopted is to be followed by the following:

Whenever possible every Nth package shall be set aside for sampling while the extract is being moved. When this is not possible, the packages shall be selected from as uniformly distributed parts of the bulk as possible.

Samples of as nearly equal size as practicable shall be taken from each package and these samples shall represent as nearly as may be, proportionally the outer and inner portions of the extract. These sub-samples shall be placed in a clean, dry closed container. When sampling is completed, the whole composite sample shall be broken up until it will pass through a sieve of 1-inch mesh; it shall be reduced to the required bulk by successive mixings and quarterings. From this bulk duplicate samples of at least six ounces shall be drawn from opposite quarters by means of a small flat scoop (and not by selecting a handful here and there). The sample shall be enclosed in the smallest clean, dry, glass receptacle, sealed and properly labeled.

NOTE:—Whenever possible the sample should be wrapped in paraffine paper and placed in the smallest straight-side glass receptacle, especially is this desirable during the warmer months of the year.

Sampling at place of manufacture shall be conducted by

running a portion from the middle of each strike into a mold holding at least two pounds. These sub-samples shall be preserved with proper precautions against evaporation, and be sampled for analysis as above.

(2) Liquid Extracts in Barrels:

The number of barrels of extract to be sampled out of any given lot shall be not less than 10 per cent. of the whole number of barrels for every 50,000 pounds or fraction thereof. The barrels to be sampled shall be rolled and shaken from end to end until the contents are homogeneous. Whenever this is not possible the heads of the barrels shall be removed and the contents stirred until homogeneous, a sample of equal size to be taken from each barrel. These sub-samples shall be put together in a suitable closed container and be thoroughly mixed. From this bulk duplicate samples of at least four ounces shall be drawn and preserved in clean, dry, glass containers; sealed and labeled with such distinguishing marks as may be necessary.

(3) Liquid Extract in Bulk:

The extract shall be agitated with air, be plunged or be mixed by some other efficient means until homogeneous. Equal samples shall then be taken from different parts of the bulk, be placed in a proper container, be thoroughly mixed and sampled as described in (2).

(4) Liquid Extract in Tank Cars:

The following methods are permissible:

a. The extract shall be unloaded into clean, dry containers and sampled according to (3); or,

b. The extract shall be mixed until homogeneous, by plunging through the dome or other effective means, then numerous equal samples shall be taken from as widely scattered parts of the bulk as possible. These samples shall then be placed in a suitable container, be mixed and sampled as in (2).

Note:—As it is almost impossible to secure a homogeneous mixture of the extract in a tank car, this method should be used only when no other is possible. Or,

c. The extract shall be sampled as follows while the car is being unloaded:—A quart sample shall be taken from the dis-

charge three minutes after the extract has begun to run; another quart sample shall be taken three minutes before the extract has all run out, and three other quart samples shall be taken at equal intervals between these two. These five samples shall be transferred to a suitable container as soon as taken, be thoroughly mixed and sampled as in (2).

(5) CRUDE TANNING MATERIALS:

A. Shipments in bags, mats or other similar packages.

A number of packages shall be sampled representing 2 per cent. of the weight for every shipment of 50,000 pounds or fraction thereof, by taking representative portions from each package. These sub-samples shall be mixed together and the bulk be reduced by mixing and quartering to the desired size. Duplicate samples of not less than five pounds each shall be preserved in air-tight containers properly labeled.

B. Shipments in bulk, bark, wood, etc., in sticks.

Sticks shall be taken from at least ten uniformly distributed parts of the bulk, be sawed completely through and the sawdust thoroughly mixed and sampled as in "A."

C. Materials prepared for leaching.

Samples of equal size shall be taken at uniform intervals as the material enters the leach and be kept in a suitable container till sampling is completed. This bulk shall then be thoroughly mixed, be reduced by mixing and quartering, and duplicate samples for analysis of at least two pounds in size be preserved in airtight containers, as in "A."

(6) SPENT MATERIAL FROM LEACHES:

Samples of spent material shall be taken from the top, middle and bottom, and in each case from the center and outer portions of the leach. These sub-samples shall be thoroughly mixed, be reduced in bulk by mixing and quartering, and duplicate samples of at least one quart in size be preserved for analysis.

(7) TANNING LIQUORS:

The liquor shall be mixed by plunging or other effective means till homogeneous and then samples of at least one pint

be taken for analysis. The addition of 0.03 per cent. of thymol or other suitable anti-ferment to the sample is essential to keep the liquor from altering its original condition.

When routine samples are taken from day to day and a composite sample analyzed, samples of equal size shall be taken from each vat after thorough mixing, be preserved in covered containers in as cool a place as possible, and be kept from fermentation by the addition of suitable anti-ferment, as above. This bulk shall be mixed till homogeneous and samples of not less than one pint each be preserved for analysis.

When a sample is taken by a member of this Association in accordance with the above method, it is requested that he state upon the label of the sample submitted and upon the analysis blank that "this sample has been taken in accordance with the official method of sampling of The American Leather Chemists Association."

C. W. NORRIS, *Chairman,*
H. C. REED,
E. J. HALEY,
T. A. FAUST.

REPORT OF THE 1913 COMMITTEE ON "OILS AND FATS."

Your committee left unfinished last year a two years' effort to develop a satisfactory method for the determination of the evaporation of mineral oils. Since the 1912 report Waters[1] has published the results of a similar investigation which was made at the Bureau of Standards. Waters obtained comparative results but found that the same weight of oil must always be heated in vessels of the same size, so that the oil surface shall always be the same in area and the convection effects of air currents be alike. A convenient vessel made of brass of the following size was found preferable: 5 centimeters internal diameter with sides three centimeters high. Waters' results together with the work previously done by this committee furnishes sufficient data whereby a satisfactory method may be developed by this committee next year.

[1] Evaporation Test for Mineral Lubricating and Transformer Oils, *J. Ind. and Eng. Chem.*, 5, 394-8.

The collaborative work done this year concerns itself entirely with sulfonated oils as the Council considered it desirable to develop methods for this class of oils as early as possible.

The following methods were therefore sent to the members of the committee and represent the developments from last year's work together with other methods, all of which it was thought would be sufficient to develop methods which would properly safeguard the purchaser of sulfonated oils.

Two samples accompanied the instructions. Sample "A" being a supposedly pure sulfonated cod oil and sample "B" the same oil containing 5.0 per cent. added mineral oil.

METHODS.

Water.

I. Weigh approximately 10.0 grams into a weighed dish containing small glass rod and about 50.0 grams previously acid washed and ignited sea sand. (Dish to be same size and shape as used in tannin determinations.) Mix oil and sand thoroughly and dry for 16 hours in oven at 95° to 100° C. Stir occasionally during drying.

II. Weigh about 50.0 grams into a 250 to 300 cc. flask and add 75 cc. water saturated xylol (prepared by heating a mixture of water and xylol with frequent shakings and subsequently removing the water in a separatory funnel). Connect with ordinary Liebig condenser. Distillation is accomplished either by direct heating or in a bath of paraffine or heavy lubricating oil, either way the distillation must not be too rapid. Distillation is continued until distillate comes in clear drops. The condenser should be washed out with a stream of xylol from a wash bottle. Collect the distillate in a tube graduated to $^1/_{10}$ cc. (Eimer & Amend show a tube for this method (No. 3,812) in their new catalogue, but it can be made from an old burette or Mohr's pipette). This tube should be set in hot water to hasten separation of water and xylol. When separated cool to temperature at which tube is graduated and read cc. of water. The percentage of water is obtained by dividing the volume of water in the distillate by the weight of oil taken.

Ash.

I. Weigh any convenient quantity into a dish or crucible. Ignite gently, allowing the oil to burn and complete incineration until all carbon is consumed.

Non-Saponifiable.

I. Weigh about 10.0 grams into a 500 to 600 cc. flask. Add 25 cc. alcohol-KOH solution (10.0 grams KOH in 100 cc alcohol) and add 100 cc. petrolic ether, B. P. 40° to 75° C. Boil with reflux condenser for 60 minutes, using a condenser having sufficient surface to prevent loss of much of the ether. Add 100 cc. water. Cool. Transfer to separatory funnel and wash ether layer with three to five portions of water of at least 100 cc. Shake out soap solution three times with ether, combining ether extracts and reserving same for subsequent washing with water. Evaporate ether extract in tared vessel. Cool and weigh.

II. Weigh 5.0 grams oil into 8-ounce Erlenmeyer flask and add five cc. aqueous KOH solution (50.0 grams KOH in water and dilute to 100 cc.). Then add 45 cc. alcohol, 25 cc. petrolic ether boiling at 70° C. and a few glass beads. Boil one hour or more with reflux condenser. Wash contents of flask into a 500 cc. separatory funnel, using both water and ether. Cool solution and shake three times with petrolic ether, using 50 cc. each time. Wash ether layer three times with 50 cc. water containing 10 cc. alcohol. Use alcohol to break emulsions. Evaporate ether extract in tared vessel. Cool and weigh.

Unaltered or Neutral Oil.

I. Weigh about 10.0 grams in Erlenmeyer flask, add 50 cc. alcohol, boil reflux five minutes and titrate with normal NaOH till permanent pink, using phenolphthalein as indicator. Then wash into separatory funnel and extract unaltered oil with petrolic ether as in non-saponifiable. (This Journal June 1913, page 241.)

II. Thirty grams dissolved in 50 cc. water, 20 cc. ammonia and 30 cc. glycerol added, and the mixture exhausted twice with petrolic ether, using 100 cc. each extraction. The ethereal solution is then washed with water as in non-saponifiable. Evaporate ether extract in tared vessel. Cool and weigh. (Lewkowitsch Vol.III, page 159.)

TABLE I.—Sample A.

	Moisture		Ash	Non-saponifiable		Unaltered or neutral oil		Total fat	Combined SO_3
	Method I	Method II		Method I	Method II	Method I	Method II		
T. A. Faust and C. Kernahan	22.44	21.00	4.7	1.50	—	—	30.72	71.05	1.70
R. H. Wisdom	22.44	20.00	4.73	—	1.75	29.10	29.69	70.05	1.66
P. A. Esten	22.93	20.41	4.88	—	1.06	28.13	30.19	69.20	1.75
C. R. Oberfell	22.8	20.6	4.7	1.7	—	30.8	31.3	69.8	1.7
Highest	22.93	21.00	4.88	1.7	1.75	30.8	31.3	71.05	1.75
Lowest	22.44	20.00	4.7	1.5	1.06	28.13	29.69	69.2	1.66
Average	22.65	20.5	4.75	1.6	1.41	29.34	30.48	70.03	1.70
Sample B.									
Faust and Kernahan	21.41	20.25	4.52	6.30	—	—	34.14	72.12	1.72
R. H. Wisdom	21.75	19.20	4.62	—	6.59	30.39	30.91	65.85	1.63
P. A. Esten	21.68	19.68	4.43	—	5.95	28.44	33.09	71.29	1.69
C. R. Oberfell	21.6	19.7	4.5	6.7	—	35.9	31.0	69.3	1.64
Highest	21.75	20.25	4.62	6.7	6.59	35.9	34.14	72.12	1.72
Lowest	21.41	19.20	4.43	6.3	5.95	28.44	30.91	65.85	1.63
Average	21.61	19.71	4.52	6.5	6.27	31.58	32.29	69.64	1.67

Combined SO_3.

I. *a.* Four grams are boiled in Erlenmeyer flask with 30 cc. dilute HCl(1:5) for 40 minutes with frequent shaking. Cool, transfer to separatory funnel and shake out with petrolic ether. Draw off aqueous layer and wash ethereal layer with water. The washings are united with main aqueous portion and the sulfuric acid determined as barium sulfate. From the amount thus found the quantity of sulfuric acid as determined below is subtracted and the difference calculated as SO_3

b. The quantity of sulfuric acid present as ammonium sulfate, etc., is found by dissolving a weighed quantity of the oil in ether and shaking out several times with a few cc. of concentrated brine free from sulfates. The several washings are united, diluted, filtered and the sulfuric acid determined as barium sulfate. (Lewkowitsch, Vol. III, page 159.)

Total Fat.

I. Ten grams mixed with 50 cc. water in flask till dissolved and solution then mixed with 25 cc. dilute HCl(1:5) and boiled five minutes. Cool, transfer to separatory funnel and shake well with 100 cc. ethyl ether. Repeat this operation with another 100 cc. of ether. Wash ether extract with water. Evaporate ether extract in tared vessel. Cool and weigh. (This Journal, June, 1913, page 242.)

The individual collaborators comment in part as follows on each of the methods proposed:

Water.

Faust & Kernahan—"The xylol method gave results 1½ per cent. lower than the sand method. We personally prefer * * * the crucible method, or * * * drying a small quantity of well mixed oil in the steam oven for several hours."

Wisdom.—"Good duplicates were obtained on both methods, but judging from results, if the xylol method is correct, it would seem that a certain amount of volatile matter other than water is driven off by the sand method."

Esten.—Prefers using small amounts of oil in the sand method. "Sulfonated oils containing ammonia will show it in the aqueous distillate. Quite evidently if the ammonia will dissolve without

changing the volume, its presence will not effect the determination, but such is not found to be the case." Mr. Esten gives the result of an experiment showing that the dissolved ammonia caused an increase in the volume of the distillate, involving an error of 0.2 per cent. "The xylol method is superior to the sand dish method; it is direct, quick and unaffected by volatile fatty acids or the volatile portion of admixed mineral oil * * * * ."

Chairman.—Evaporation at 95° to 100° C. is not a true indication of the water content for varying amounts of volatile matter other than water are driven off. The xylol distillation method is not an elaborate method, but is susceptible of easy and rapid execution.

Ash.

Chairman.—The results for ash by any method are so satisfactory as to require no special comment.

Non-Saponifiable.

Chairman.—Satisfactory results were obtained by both methods, so that either is suitable, although it is likely that a water solution of KOH is preferable on account of keeping qualities. Some question is raised on the advisability of having ether present during saponification, but by the use of ether in this way and a few glass beads troublesome bumping is entirely prevented and the extraction can be conducted with less probability of troublesome emulsions forming.

Unaltered or Neutral Oil.

Faust & Kernahan.—"Neither method is accurate, although method 2 gave more satisfactory results than method 1."

Wisdom.—"Of the two methods the reporter much prefers method 1 not only for greater ease in operation, but also for better duplicates. Method 2 involves considerable technique in order to obtain anything like satisfactory results."

Esten.—Method 1.—"Washing the combined extracts with 50 per cent. alcohol gives quicker results." Method 2.—"produces persistent emulsions, requiring 12 or more hours for separation of the ether layer. If smaller quantities of sample,

water, glycerol and ammonia were used, the determination would doubtless be quicker and more efficient."

Chairman.—Both methods are unsatisfactory, due to difficulty in washing free from soap and the liability to form persistent emulsions Method 2 designed by Lewkowitsch for sulfonated castor oil is plainly not suited to the sulfonated fish oils. Method 1 may by modifications prove servicable.

Combined SO_3.

Chairman.—The results returned mark the method as very accurate. As to the value of this determination for the valuation of oils there is some question, since the SO_3 is not entirely combined with a fatty acid radical, but may also be in combination with glycerol. However, if this determination is required the method used is satisfactory.

Total Fats.

Chairman.—The method used gives as concordant results as any perhaps, but as pointed out by Mr. Esten the use of a smaller quantity might be advantageous.

The controversy on total fats rests largely on whether the total fat shall be determined directly by a similar method to the one used by this committee, which gives the total fatty acids plus the non-saponifiable or whether it shall be estimated by the difference between 100 per cent. and the sum of the ash, water and non-saponifiable, or in other words, a figure representing the original fatty glyceride instead of the free fatty acids and the non-saponifiable. On this point Esten and Wisdom of the committee are in favor of the direct determination while Faust, Kernahan and the chairman favor the proximate analysis.

Any method for the direct determination depends on the complete splitting off of the sulfuric radical, if not, the part not decomposed is washed out. This is a difficult matter and will probably always be the cause of non-agreement in results.

Table II. shows the total fats and total fatty oil as obtained by the direct determination and by difference using the results for water by both the sand and distillation methods. As the sand method obviously estimates volatile matter other than water the total fatty oil using this method is erroneous. When, as in

TABLE II.—Sample A.

	Faust and Kernahan	Wisdom	Esten	Oberfell
Total fats, direct determination	71.05	70.05	69.20	69.8
Total fatty oil (difference), using moisture by sand method	71.36	71.08	71.13	70.8
Total fatty oil (difference), using moisture by xylol distillation method	72.08	73.52	73.65	73.0
Sample B.				
Total fats, direct determination	72.12	65.85	71.29	69.3
Total fatty oil (difference), using moisture by sand method	67.76	67.04	67.94	67.19
Total fatty oil (difference), using moisture by xylol distillation method	68.93	69.59	69.94	69.12

sample "B" where mineral oil is present the value obtained by difference is the fatty oil and not the fatty acids plus the non-saponifiable which includes the mineral oil. Obviously what the tanner is using and for what he should pay is the total fatty oil.

The following is suggested as a specification basis for the purchase of sulfonated oils:—The standard shall be 70 per cent. *Total Fatty Oil.* Any oil tendered which tests 71 per cent. total oils or over, shall be paid for at a pro rata increase, calculated as from the 70 per cent. standard. Any oil which tests under 70 per cent. but is 68 per cent. or over shall be subject to a reduction of one and one-half times the shortage calculated at pro rata price as from 70 per cent. If test falls below 68 per cent. the buyer shall have right of rejection.

Recommendations.

That the methods used by this committee for water, (xylol distillation), ash, non-saponifiable (Method II preferable) and combined SO_3 be the provisional methods.

That the calculation be made for the total fatty oil by the difference between 100 per cent. and the sum of the water, ash and non-saponifiable.

That the method for unaltered or neutral oil be further investigated.

That the results obtained by these provisional methods be reported only in one decimal place.

CHARLES R. OBERFELL, *Chairman.*

Harrisonburg, Virginia,
November 13th, 1913.

REPORT OF THE COMMITTEE ON "COLOR TESTING."

By J. M. Seltzer, Chairman.

The work that was done by the Committee on "Color Testing" last year was claimed by the chairman to have been very unsatisfactory and it was suggested by him that in order to obtain results on the valuation of tanning materials some other method than that of using skins would have to be used, such as tintometer readings and cotton or paper impregnated with gelatine.

The author of this report was appointed chairman of the Committee on "Color Testing" by the Council at the meeting held September 6th, 1913, and in order to find out what methods or ideas should be followed, the following questions were asked those who signified their willingness to serve on this Committee: What class of skins do you think should be used in this work on "Color Testing?" What has been your experience in regard to the "Value of Tintometer Readings" on tannin solutions, the "Armstrong Method of Color Testing," the use of lightly chromed leather and the use of animalized cotton or paper for the purpose of Color Testing?

The replies received were as follows:

F. H. SMALL:

"I have, as yet, failed to find any convincing reason for giving up the practice of color testing, which I have followed for a number of years; that is, using a cow grain split. I believe the color developed on these splits is more informative than that on sheepskin or calf, and I see nothing to be gained by the use of an under-grain split, since, if one prefers the texture of such, he will find it on the under surface of the grain split.

"From my personal experience, and what I saw of the work of last year's Committee, I believe the method of tanning the

skiver and the strength of the tanning solution used are comparatively immaterial; that is, that the final color is affected very little by these parts of the process. I do believe that the preliminary preparation of the skin and the washing given the skiver after the tannage are much more important, and that, if the Committee sees fit to do further work with grain splits, the experimentation should be devoted to these two steps in the process.

"As I have so many times stated, I do not believe the practical leather man will ever be satisfied with a color valuation of extract which does not give him a piece of tanned hide of some sort or other which he can examine. While, therefore, the tintometer, or cloth, or animalized paper may be of assistance to the extract manufacturer, or to the chemist who is trying to determine the color uniformity of different shipments of extract on the same contract, I do not believe any one of these methods will be generally acceptable.

"The grain splits which I use in the laboratory here for color testing are, when received, placed in a regular boro-phenol solution, digested for sometime, transferred to fresh boro-phenol, and, if necessary, to still a third fresh solution, or until the solution remains acid to litmus after the split has been digested in it for, at least, twenty-four hours. Portions of the split to be used for color testing are soaked in luke-warm water which is changed at more or less frequent intervals, that is, say every fifteen minutes, until the sample has no distinct odor of phenol. It is then placed in a tanning solution which is ordinarily of approximately one-half per cent. strength: at the end of perhaps five hours transferred to a solution one per cent. strength and at the end of another similar period to a solution of five per cent. strength. In this last solution it remains until fully tanned. This requires usually twenty-four to thirty-six hours. The whole tannage usually occupies about two days time.

"As stated above I do not regard the exact details of the tanning process as of much importance so long as the skiver is fully tanned and is topped off in a reasonably strong liquor. The washing of the tanned skiver is, however, of decided importance and must be given careful attention in order to secure

uniform and concordant results. The tanned skiver should be soaked in luke-warm water, squeezed out, again soaked, and so on until when churned for fifteen minutes in approximately 500 cc. of luke-warm water the water remains practically colorless. To prevent a darkening of the skiver from the effect of the air, it may be desirable to oil the grain but this must be done with care and only a minute amount of oil used. The drying should be conducted in a cool, dark, well ventilated place.

"It is difficult to prescribe a definite procedure for preparing the skiver or for washing it as, in either case, the procedure will need to be varied with the thickness and texture of the skiver. I have tried, therefore, rather to suggest what may be called 'end values,' or 'end points,' rather than exact methods of attempting to secure the same."

R. H. WISDOM:

"With my experience in color testing and the reception accorded the present provisional method, I feel it will be impossible to induce any tanner to accept color tests other than those on pelt, or at least where hide substance is the prevailing factor, such as Dr. Gansser's animalized cotton test. Such being the case, it is up to us to discover or invent a method which will approximate tannery results, and at the same time give concordant laboratory tests.

"I have had considerable success in using selected portions of selected skins, and I think we can show a great improvement if we have a method similar in effect to the proposed official method for extracts, regulating every step in the process, such as time, temperature, strength of liquors, etc. As has been suggested, if we could but have a standard source of supply, where only selected skins would be obtained, such as our hide powder supply, this also would aid materially in solving the problem.

"The writer has had little or no experience with the undergrain split, but prefers the sheepskin to the cow grain split for evenness of color. In regard to tintometer readings, while they no doubt have considerable value from a scientific standpoint, it is doubtful if they will ever come to be recognized in a commercial way by the trade in general. As to the Armstrong method, it certainly is worthy of trial by the Committee. Light-

ly chromed leather and animalized cotton or paper have as yet not been tried out in this laboratory."

L. M. Richeson:

"I think the cow grain split is by far the most desirable class of skins which should be tried out by the color testing committee, providing they could be bought at a reasonable figure and a source of supply could be obtained. In using the cow grain split in color testing, we arrive at conditions more nearly like those of the tannery.

"I do not know anything about the use of lightly chromed leather for color testing but I should like very much to see it tried out by the committee, the fact that the skin has been lightly chromed would cover the defects in the skin, giving a more uniform color, thus enabling two laboratories to get better agreement in their color tests. Several times I have seen color tests on the same extract made by three or four laboratories and it is the rarest thing that you see any two which are alike. Doubtless you recall that this is the experience that last year's committee had.

"The writer thinks it would be a waste of time in trying the tintometer reading on extracts or the use of animalized cotton or paper. In the first place, the tanner wants his color tests made out of material more nearly like leather, and again these two methods have been tried out by many different authorities and in every case they have been proven to be unsatisfactory.

"I have done some little on the Armstrong method of color testing and I think it would be worth while for the committee to investigate this method. I tanned several pieces of skin which Mr. Armstrong sent me several months ago and got very encouraging results from them. If this method should be tried by the committee, the writer would like to suggest the use of denatured alcohol as it is cheaper and I see no reason why it will not do the work just as well as the pure alcohol."

A. W. Hoppenstedt:

"The method we use for making color tests of extracts is, to make up a solution of approximately five per cent. solids and to tan the piece of skin over night in this solution. If the skins are not tanned in the morning they are left in the solution

until they are tanned, but it is very rarely that skins require a longer time than over night. The skins after tanning, are washed out thoroughly under the tap, squeezing them out between the washings and then finally washed on the shaker for fifteen minutes. After washing, the skins are slicked out and tacked. For tanning materials other than extracts, we weigh out 50 grams of the material and add to this, 500 cc. of distilled water at 80° C. After stirring the mixture thoroughly, we allow it to cool and then tan the skin directly in the same.

"In regard to the whole sheep skins which we use, as compared to a skiver, I would like to say that I have found that the whole sheep skin gives a color test which compares very closely with the color obtained in the tannery on heavy hides."

It is the opinion of the chairman that the "value" obtained by the "tintometer reading" indicates to a certain degree the comparison between different shipments of the same manufacturer's extract, but does not indicate what may be expected in the practical working of that extract, neither does it enable an operator to form a correct comparison between different brands of extract. Some extracts may be dark in color when examined through the tintometer and at the same time produce a light color on leather. The tintometer has been in use for a number of years in this laboratory and has not furnished very much information from the tanner's point of view. It is the opinion of the members with whom the chairman corresponded and also that of most of the leather trade in general that nothing indicates the color value of an extract as well as a test made on pelt. Therefore the chairman decided that the Committee should experiment once more to find some means of obtaining satisfactory results on animal skins.

The directions which follow were sent to:

Mr. F. H. Small, Graton & Knight, Mfg. Co., Worcester, Mass.

Mr. R. H. Wisdom, Stamford Mfg. Co., Stamford, Conn.

Mr. P. M. C. Armstrong, Armstrong Tanning Co., Detroit. Michigan.

Mr. L. M. Richeson, England, Walton Laboratory, Harrisonburg, Va.

The materials sent were a sample of liquid chestnut extract

28.35 per cent. tannin. Pure cod liver oil for oiling tests. One piece whole sheep skin preserved in boro-phenol solution. This skin was selected from the highest grade of light lambs by Mr. A. W. Hoppenstedt.

One piece "cow grain split" marked No. 1.

One piece "cow grain split" marked No. 2.

These skins were also preserved in boro-phenol and were furnished by Mr. F. H. Small. These skins were taken from different animals and the tests were made in order to show what variation would take place between different hides. Skin No. 1 had a reddish cast, while skin No. 2 was almost perfectly white. It is probable that these two skins represent the extremes which might be expected from cow grain splits.

Directions for Committee on "Color Testing."

NOTE:—All temperatures throughout are to be 20° to 25° C., unless otherwise stated. All water used is to be distilled. Dissolve extract in water at 50° C.

Preliminary Treatment of Sheep Skins.

Method No. 1.—Preparation by means of fermented bran drench. To 15 grams bran add 100 cc. water (50° C.), put mixture in a warm place for 48 hours, after which dilute with 200 cc. water, when the drench will be ready for use. Start this preparation in the morning and in the afternoon of the same day place five pieces of sheep skin, size two inches by three inches in water for 24 hours, changing the water and squeezing the skin frequently to remove all traces of boro-phenol, after which put the skins in 300 cc. one per cent. borax solution (40° C.) until the following morning, wash in two changes of water (40° C.) and put skins in the bran drench for the rest of the day. Wash in two changes water, (40° C.), when the skins will be ready for tanning.

Method No. 2.—In the afternoon following the day that the above sheep skins were put in water, place five pieces, size two inches by three inches in water for 24 hours, changing the water and squeezing the skins frequently to remove all traces of boro-phenol. Mark these skins in order to distinguish them from those treated with the bran drench.

Methods of Tanning and After Treatment.

Tan one piece of each of the above treated skins in the same solution by the following methods: Two hundred cc. of solution should be employed in each instance and tanning should take place at 20° to 25° C.

A. Shake 10 minutes in ½ per cent. tannin solution.
Shake 10 minutes in 1 per cent. tannin solution.
Shake 10 minutes in 2 per cent. tannin solution.
Lay away in 2 per cent. tannin solution for 16 hours.

Wash in four changes of water, 358° C., with repeated squeezing to remove the excess tan liquor, soaking 10 minutes between each washing, slick, tack on board, slightly oil one-half of each test with cod oil, place in a dark cool place to dry.

B. Shake 10 minutes in 1 per cent. tannin solution.
Shake 10 minutes in 2 per cent. tannin solution.
Shake 10 minutes in 4 per cent. tannin solution.
Lay away in 4 per cent. tannin solution for 16 hours.
Wash and proceed same as in A.

C. Lay away in 1 per cent. tannin solution for 16 hours.
Wash and proceed same as in A.

D. Lay away in 2 per cent. tannin solution for 16 hours.
Wash and proceed same as in A.

E. Lay away in 3 per cent. tannin solution for 16 hours.
Wash and proceed same as in A.

Armstrong Method for Preparing Color Tests.

Place six pieces of sheep skin two inches by three inches and the same number pieces of the cow grain split No. 1 in water for 24 hours, (start in the morning), changing the water and squeezing the skins frequently, after which put the skins in one-fourth of one per cent. sodium hydroxide solution for two hours. Wash the skins one time in water and put them in a wide mouth bottle containing one-tenth of one per cent. solution of pure ammonium chloride, which should be alkaline to methyl orange but not to phenolphthalein, for 24 hours. Use plenty of solution at least one liter for every square foot of skins. Shake vigorously, occasionally and test once in a while with phenolphthalein. If the slightest redness appears, add a few drops of dilute hydro-

chloric acid, but not enough to make the solution more than slightly acid to methyl orange. Pour off the solution and rinse rapidly three or four times with water (35° C.), fill bottle half-full of water (35° C.) and shake vigorously. Let stand one hour, change water and let stand another hour and test the water for chlorides with silver nitrate. If there is a test take fresh water (35° C.) and let it stand another hour after shaking. Repeat this washing until the water gives no test for chlorides. Drain off the water and completely cover the skins with 95 per cent. alcohol. Let stand until morning. Pour off the alcohol and take new alcohol, shake and let stand 24 hours. Pour off the alcohol and cover skins with ether. Let stand until evening. Place skins in new ether for 24 hours when the skins will be ready for tanning.

Methods of Tanning and After Treatment.

Take one of each of the above treated skins by the following methods: Two hundred cc. of solution should be employed in each instance.

F. Place in a 2 per cent. tannin solution (45° C.) for 2 hours.

Wash in four changes of water (35° C.) with repeated squeezing to remove excess of tan liquor (soaking 10 minutes between each washing) slick, tack on board, slightly oil one-half of each test, place in a dark, cool place to dry.

G. Place in a 2 per cent. tannin solution (45° C.) for 4 hours. Wash and proceed same as in F.

H. Place in a 2 per cent. tannin solution (45° C) for 16 hours. Wash and proceed same as in F.

I. Place in a 3 per cent. tannin solution (45° C.) for 2 hours. Wash and proceed same as in F.

J. Place in a 3 per cent. tannin solution (45° C.) for 4 hours. Wash and proceed same as in F.

K. Place in a 3 per cent. tannin solution (45° C.) for 16 hours. Wash and proceed same as in F.

NOTE:—Treat six pieces of cow grain split No. 2 same as described above.

METHOD OF USING COW GRAIN SPLITS FOR COLOR TESTING.

Method No. 1. Place three pieces of skin No. 1 (2 inches x

3 inches) in water for 24 hours, changing the water and squeezing the skins frequently to remove all traces of boro-phenol.

Place three pieces of skin No. 2 (2 inches x 3 inches) in water and treat same as above.

Method of Tanning and After Treatment.

Tan one piece of each of the above treated skins by the following methods: Two hundred cc. of solution should be employed in each instance and tannage should take place at 20° to 25° C.

L. Shake 30 minutes in ½ per cent. tannin solution.
Shake 30 minutes in 1 per cent. tannin solution.
Shake 30 minutes in 2 per cent. tannin solution.

Lay away in two per cent. tannin solution for 24 hours. Wash in four changes of water at 35° C. with repeated squeezings to remove the excess tan liquor, soaking 10 minutes between each change. Slick, tack on board, oil one-half of each test with cod oil. Place in a cool, dark place to dry.

M. Shake 30 minutes in 1 per cent. tannin solution.
Shake 30 minutes in 2 per cent. tannin solution.
Shake 30 minutes in 4 per cent. tannin solution.
Lay away in 4 per cent. tannin solution for 24 hours.
Wash and proceed same as in L.

N. Lay away in 1 per cent tannin solution for 3 hours.
Lay away in 2 per cent. tannin solution for 3 hours.
Lay away in 3 per cent. tannin solution for 24 hours.
Wash and proceed same as in L.

Method No. 2. Place four pieces of skin No. 1, (2 inches x 3 inches) in water at 35° C., change water at frequent intervals, about every 15 minutes, until the samples have no distinct odor of phenol.

Treat four pieces of skin No. 2 (2 inches x 3 inches) in water (35° C.) and proceed same as above.

Method of Tanning and After Treatment.

Tan one piece of each of the above treated skins by the following methods:

O. Lay away in ½ per cent. tannin solution for 4 hours.
Lay away in 1 per cent. tannin solution for 4 hours.
Lay away in 3 per cent. tannin solution for 24 hours.

Wash in water, at 35° C., with repeated changes and squeezing until when churned for 15 minutes in water at 35° C., the water remains practically colorless. Slick, tack on board slightly oil one-half of each test and place in dark place to dry.

P. Lay away in ½ per cent. tannin solution for 4 hours.
Lay away in 1 per cent. tannin solution for 4 hours.
Lay away in 3 per cent. tannin solution for 36 hours.
Wash and proceed same as in O.

Q. Lay away in 3 per cent. tannin solution for 24 hours.
Wash and proceed same as in O.

R. Lay away in 3 per cent. tannin solution for 36 hours.
Wash and proceed same as in O.

S. If any sheep skin or cow grain split remains after doing the work outlined, prepare color tests according to the method in use at your laboratory, using extract sent you. Give description of process.

T. Treat, tan and wash any remaining skin by any method you may wish to try in comparison with the ones outlined. Give description.

How to Mark the Color Tests.

Mark each test, in the upper left hand corner, in small letters as follows: Mark all sheep skin tests by letter of method and after that, mark letter of your name in order to distinguish the tests from those of the other collaborators.

Mark cow grain split tests No. 1 with letter of method, 1, and letter of your name. Mark cow grain split tests No. 2 with letter of method, 2, and letter of your name. Send in any comments that you may wish to make.

Description of Various Color Tests.

Since the tests prepared by the different members cannot be shown through the Journal the chairman will make an attempt to describe the agreement and disagreement in the work of the different collaborators.

The work of each member will be marked as follows:—

1—Small, 2—Wisdom, 3—Richeson, 4—Armstrong, 5—Seltzer.

Method No. 1.—Furnished unsatisfactory results throughout, no agreement whatever.

Method No. 2.—

A. 1-2-5 agree well, 3 is darker, while 4 is lighter.
B. Colors agree fairly well.
C. Agree fairly well, tests undertanned.
D. Fair agreement.
E. Close agreement.

Mr. F. H. Small in addition to the work outlined for sheep skins prepared tests from a skin of his own selection. These tests are lighter in color than the others and do not show much difference in color by Methods No. 1 and No. 2.

Analyst No. 3 obtained black, hard and bony tests by Method No. 1 and were entirely off from those of all the other collaborators.

F. to K. Sheep skins are entirely unsatisfactory.
F. to J. Cow Grain Splits are undertanned and show no good agreement.
K. Cow grain Split. While these tests are not absolutely uniform in color they agree fairly well with the exception of the work of Analyst No. 1.
L. Fair concordance.
M. Fair concordance.
N. Close agreement.
O. Fair agreement, No. 1 being dark.
P. Fair agreement, No. 1 being dark.
Q. Fair agreement, No. 1 being dark.
R. Fair agreement, No. 1 being dark.
Cow grain split No. 1 gave darker colors than No. 2 throughout.

Comments.

F. H. Small:

I increased the number of tests made from those called for by using a second sheep skin for all the tests where sheep skins were called for. The tests marked S1 were made with the sheep skin sent and those marked S2 with a skin from my own stock. The work was largely done by Mr. V. J. Mlejnek and the following comments represent his views and those of the writer.

Method No. 1.—The treatment with borax as prescribed is altogether too severe, the skivers being plumped excessively. This alkali plump is removed by the bran drench and the skins fall only to plump again excessively from the acid of the drench. All the skivers prepared in this way were strongly acid when put in the liquor. The tanned skivers prepared by this method are uneven in color and the skivers from the two skins differ decidedly in appearance. This method of preparation, as outlined, is most unsatisfactory, leading to variable and divergent color results.

Method No. 2.—This is satisfactory—skivers from both skins showing good agreement.

The several methods of tannage, A to E, apparently affect the color value little, if at all. Two hundred cc. of a 1 per cent. or 2 per cent. solution was insufficient for complete tannage of the amount of skiver used,—the skivers coming out only partially tanned and the liquors being so sapped as to show a much weakened color. Either B or E would seem a satisfactory procedure.

Oiling sheep skins is of doubtful value.

Armstrong Method.—Little success was attained with this method,—possibly due to inexperience,—possibly to failure of some of the details of the procedure to be suited to the conditions. For instance,—the treatment with sodium hydroxide solution would seem to have been uncalled for. The skivers were plumped beyond all reason by this treatment, and while they fell in the ammonium chloride bath to more or less normal and excessive plumping of this sort usually makes trouble in the subsequent working of the skins.

The skivers when put in the warm liquor color very rapidly and considerable care is necessary to set an even color. After the first little while the tannage seems to progress comparatively slowly. None of the skivers in the two or four-hour tannages were tanned through and some of the sixteen-hour skivers show some rawness. Sheep skins prepared by this method set a color in these tests much heavier than usual and more like the normal color of a grain split. Possibly shaking instead of laying away would give better results.

Of the two methods given for preparing cow grain splits the Method No. 1, so far as the results of this test go, would appear preferable. All the samples prepared in this way came out well and of uniform shade. Samples prepared by Method No. 2 were in general darker and of less satisfactory uniformity.

As regards the several methods of tanning, all lead to essentially the same color value. L., M. and N are practically indistinguishable. Similarly O, P, Q and R are alike save that Q and R show a somewhat coarser, harsh grain.

The general conclusions to be drawn from this series of tests would seem to be, therefore,—first, skivers should be preserved for use in boro-phenol solution. Second, they should be prepared for use by soaking twenty-four hours in water, the water being changed and the skivers squeezed at frequent intervals during this time. Third, the method of tanning is comparatively immaterial. A 3 per cent. or 4 per cent. solution at least is desirable to secure complete tannage. Sheep skin may be put directly in a solution of this strength, but cow grain is preferably started in weak solutions as by method L., M or N.

R. H. WISDOM:

Sheep Skins.

Judging from the unoiled portions, the fermented bran drench, with the exception of Test D, appears to give slightly darker shades. The reporter is not in favor of any method which tends to darken the skins. The oiling process while showing darker in every instance, is not uniform and the shade apparently depends upon the amount and manipulation of the oil. Test A and B plainly show the effect of drumming but it is doubtful if such a method will ever become popular among laboratories where a large amount of color testing is required. Tests C and D are undertanned and respond very slowly to the softening process. Test E is to the reporter, the most desirable.

Cow Grain Splits.

In comparing the two methods, No. 2 has a decided advantage in time and also gives lighter shades. Unlike the sheep skins, the effect of the oiling is quite the reverse, giving somewhat lighter and clearer tones. Skin No. 2 gives lighter shades in every in-

stance. There is little to choose between tests L and M, the shades being very similar. N gives a somewhat darker test. Tests O, P, Q and R show fairly good uniformity. Cow grain split seems to hold little advantage over sheep skin in uniformity of different skins.

Armstrong Method.—The reporter is keenly disappointed in his results on this method. As laid down in the committee work, it is evidently not adapted to sheep skin, for in no instance could the reporter secure a presentable test. The results on the cow grain splits were somewhat better—considerably so on Tests H and K (16 hours duration) which compare very favorably with the regular cow grain splits. The oiling here helps considerably, both in lightening the shade and bringing the two skins closer in uniformity. However on all the short time tests very unsatisfactory results were obtained. Taking it altogether the results herewith shown do not warrant the immense amount of time required to prepare the skins and the reporter unless able to secure much better results on future tests, is not in favor of this method in its present form.

Laboratory Method.

Preparation of Skin.

The skins tanned under Test S were prepared in a manner similar to Method No. 2 for cow grain splits which most closely conforms to the method used in this laboratory.

Method of Tanning and After Treatment:

Lay away for one hour in weak solution consisting of 10 cc. 20 degree barkometer liquor diluted to 150 cc. at 20° to 25° C. Lay away over night in 150 cc. approximately 20 degree barkometer liquor at 20° to 25° C. This liquor is dissolved at 80° C. Wash under tap, slick, tack on board and set in cool, dark place to dry. Test X is color test on sheep skin prepared in this laboratory and tanned as above.

Summary.

As to the proper substance to use for color testing, it seems to the reporter that this question should be settled by the tanner. If he wishes simply to make comparative tests, there is nothing

in the opinion of the writer like sheep skin. Quoting from a letter to your Chairman under date of February 3rd, 1913, "I have had considerable success in using selected portions of selected skins, and I think we can show a great improvement if we have a method similar in effect to the proposed official method of extracts, regulating every step in the process, such as time, temperature, strength of liquor, etc. As has been suggested, if we could but have a standard source of supply, where only selected skins would be obtained, such as our hide powder supply, this also would aid materially in solving the problem."

Certainly the results shown in the tests on a comparison of two different skins, are much in favor of the sheepskin for uniformity. If, however, the tanner wishes to approximate the actual color returned from his tan-yard; naturally he wants to use the same kind of skin he is working with. However, the reporter believes that the two skins used in the Committee work (sheep and cow grain split) would cover the ground satisfactorily. As to the method of preparing the skins for tanning, the reporter believes every step in this process should be regulated and the simpler the process, the better. In regard to method of tanning, the same remarks apply. Judging from the reporter's results, the elaborate washing of the tanned skin is hardly worth while. A simple washing in any good water appears to be all that is necessary. As to oiling, it seems to be a matter of which skin is used.

L. M. RICHESON:

There was evidently something wrong with one lot of the sheep skins, as you will note the ones that went through the bran drench are very dark and appear as though they were burnt. We prepare all of our sheep skins for color testing by means of the fermented bran drench and we never have any trouble in getting a nice, clear piece of skin for color tests. My tests fall a little short of the desired measurement but the writer had to cut the skins small in order to get the required number of tests, from the skins which you sent me. In looking over the tests, there seems to be a great variation in color which is hard to account for.

From my results I cannot see that the Armstrong Method

gives a uniform color. You will note that some of the cow grain splits treated by this method are much lighter than others and what the Association is after is to obtain a method which will give a color more like the color obtained in the tannery.

The color test marked "L-S-R" is a piece of the cow grain split No. 1 and was tanned by the method of color testing used in this laboratory. This test gives a color which resembles very closely the color that chestnut extract gives in the tannery.

From the work done this year and having seen Mr. Oberfell's results last year, the writer's conclusion is that cow grain splits preserved in boro-phenol, are the most satisfactory skins to use for color testing. That is, provided an available supply can be obtained at a reasonable cost.

I think they should be tanned in not less than a one per cent. solution nor more than a two per cent. solution of tannin and should be allowed to stand from 12 to 16 hours, shaking about 30 minutes when skins are first put in and 10 to 15 minutes before taking out.

Method of Color Testing Used in E. W. C. Laboratory.

Start at four in the afternoon, dissolve 15 cc. of extract in 400 cc. of water, put in piece of sheep skin, shake 30 minutes and allow to stand until the next morning. Shake about 10 minutes the next morning, thoroughly wash in warm water until water is colorless. Place color test on a towel to dry, work out test occasionally in order to insure a soft, pliable color test.

P. M. C. Armstrong:

I have been obliged to omit methods L to R inclusive, as I have not had an opportunity to fit up a shaker. I also omitted Method J by mistake and have not yet had the opportunity to do it.

All methods involving the use of sheep skins I have found quite unsatisfactory, as the color obtained is entirely too light. One of the complaints I have always had against the usual method of color testing is that the color shown by the skiver does not represent the color shown in the tanned leather. I note that you state that the skins prepared by the "Armstrong" method were all darker than those by other methods. I ex-

pected this and consider the fact a distinct advantage, although it probably would not meet with the approval of the extract manufacturers, who wish to have their extracts show up as well as possible. I am enclosing in this letter a sample of our tanned stock, and also a color test made with some of our yard liquors, which will show you the accuracy of the alcohol and ether method. Even here you will observe that the color shown is a trifle lighter than that of the tanned stock. How much more, therefore, would be the variance with the method in general use of making pickled sheep skin color tests? I believe that, whatever method be adopted, sheep skins should be barred, and all testing be made on cow grains.

I am not surprised to learn that you found considerable variation in the reports from the different members of the committee, on the alcohol and ether method. The percentage of NaOH which you recommend is so great that it is quite impossible to remove it uniformly with ammonium chloride. You recommend the use of one-fourth per cent. NaOH, which you will see is just twice as strong as the saturated lime water which would normally be in the hide coming out of the lime; also, sodium hydroxide is so vastly stronger than calcium hydroxide that it is necessary to use it in very great dilution, not more than one in 10,000. In any event, ammonium chloride will not remove sodium hydroxide from the skin unless used in tremendous concentration. I followed the method recommended by you exactly, and I found that it was impossible to remove the sodium hydroxide from the center of the skiver, no matter how much ammonium chloride was used. I have taken the liberty, therefore, of preparing some of your cow grains in a saturated solution of lime instead of NaOH, and will send them to you in a few days. I do not know what previous treatment the cow grains have had, but I cannot detect any trace of sulphates or oxalates, and I fancy that soaking them in lime water should return them to the same condition they were in when they came out of the lime.

You will pardon me if I give it as my opinion that the committee work done on the alcohol and ether method, using one-fourth per cent. NaOH, is totally valueless. I am sending you

under separate cover some reprints of the original article, and I would consider it a favor if you would distribute them to the other members of the committee with the request that they test the method exactly as described. I am also enclosing a reprint in this letter with some notes which may be of assistance. I do not wish to appear to extol my method of color testing, but if you will examine the enclosed sheet showing the two different pieces of leather, I think you will be convinced that it should be investigated further before adopting any other method. I cannot emphasize too much the necessity of having the color test resemble the color of the leather which would be tanned in the material in question, and any method which gives a lighter color than the leather would have when tanned is deceptive. For this reason I believe that color tests should not be oiled, as oil almost invariably bleaches leather somewhat. If they are washed free from excess tan it is unnecessary.

J. M. SELTZER:

Sheep Skins.

Method No. 1.—The tests made according to this method of preparation, while perfectly uniform in regard to color are considerably darker than those prepared by Method No. 2. There is practically no difference in color caused by the different methods of tanning with the exception of test C, tanned in one per cent. solution for 10 hours, which is undertanned and darker in color than the other four tests. This method does not give a satisfactory test with the whole sheep skin used in this work. The chairman has been using this method for preparing light sheep skivers for color tests in this laboratory with satisfactory results when the skins prepared according to Method No. 2 failed to give anything but a spotted, dark and ununiform color. Oiling darkens the grain on sheep skins and is unnecessary.

Method No. 2.—These tests are light in color and show practically no difference by the different methods of tannage, test C being a shade darker than the rest, due to undertannage. This is a desirable method for sheep skins if they do not contain too much grease.

Armstrong Method.—The sheep skins prepared by this method are entirely unsatisfactory probably due to the solution of sodium hydroxide used being too strong. The chairman prepared light sheep skivers according to the method described above and obtained satisfactory results, therefore, suggested the same strength in the committee work, but found out later that it did not work well with whole sheep skins.

The cow grain split No. 1 was darker than No. 2 in all instances. All these tests are incompletely tanned with the exception of K, tanned in three per cent. solution for 16 hours. In this work it was found that the darkest colors were obtained in the skins in which the least tannage had taken place and vice versa. It is necessary to oil the tests when using cow grain splits since the oiled portions are lighter and more even in color in all cases. Test K is the most satisfactory one by this method and compares well with the regular cow grain method.

Cow Grain Split Method.

Here again are the tests made from skin No. 1 darker than those from No. 2. Tests L, M, O, and P, are about the same shade while tests N, Q, and R, compare well with each other but are much lighter than those of the other four lots. The tests prepared according to N are probably the best for evenness of color. The oiled portions are lighter in all instances on skin No. 2 but does not affect skin No. 1 very much. In the work that the chairman did on sheep skins and also on cow grain splits it was noticed that all tests must be thoroughly tanned and a three per cent. tannin solution seems to give the best results in all cases. If the test is undertanned it is darkened to a considerable degree and gives a hard, harsh piece of leather. Sheep skins may be tanned direct in a three per cent. tannin solution but cow grain splits should be tanned through a graded solution such as Method N. Oiling the tests should be followed on cow grain splits but not on sheep skins. It is necessary that the boro-phenol solution must be thoroughly washed out of the skins before tannage and also the excess of tannin solution after the skins have been tanned. In the work that the chairman did on this committee and on personal work done, there seems to be no decided advantage to offer for the Armstrong Method. The

colors seem to be about the same as those tanned without this treatment, when the skins are thoroughly tanned. Light sheep skivers were tanned by the Armstrong Method, and also by the bran drench method and the tests were indistinguishable.

CONCLUSIONS.

All skins should be washed in water at 20° to 25° C. for 24 hours, squeezing frequently to remove all traces of boro-phenol solution.

Tannage should take place in a three per cent. tannin solution, direct for sheep skin and graded for cow grain splits, the duration of tannage should be 16 hours for the former and three hours in one per cent. solution, three hours in two per cent. solution and 24 hours in three per cent. solution for the latter. All tests should be thoroughly washed in four changes of distilled water at 35° C., digesting 10 minutes between each washing and squeezing frequently to remove excess tannin solution. Sheep skins should not be oiled while cow grain splits should be oiled.

SUMMARY OF RESULTS.

The matter of "Color Testing" seems to be a hopeless task and it is doubtful if a method will ever be found by which different analysts can obtain the same results. While the results obtained by this work are fairly good in some instances, absolute concordance is not found in any case. The work shows that different lots of hides will give varying results, as will different analysts using the same skin. Probably the difference in hides could be reduced to a minimum if all members would obtain the skins from a central source and that central source would endeavor to supply only selected lots as nearly alike as it would be possible to furnish them. Mr. A. W. Hoppenstedt has been furnishing some members with selected light lamb sheepskins for some time and says it would be possible for him to furnish them to all of the Association Members, if they so desire. The writer has not asked Mr. F. H. Small as yet, but probably he could furnish the cow grain splits on the same condition as above stated. It remains for the Association to decide whether they prefer "Sheep

skins" or "Cow Grain Splits" for use in the work on "Color Testing." From the results obtained, the sheep skin seems to show the most concordant results, but can the tanners form any idea by that test of what he may expect from a certain extract in the tan-yard? Most of the members of the committee think not, however the sheep skin will show comparative results on extracts and the only way to satisfy both extract maker and tanners would be to adopt the suggestion of Mr. Wisdom, that is using both sheep skin and cow grain split, which would cover the ground satisfactorily.

Several analysts recommend three per cent. tannin solution, one recommends three to four per cent. solution and one one to two per cent. solution for this work. Several members prefer cow grain split skins to sheep skins, while one of them thinks sheep skin should be barred entirely. Oiling cow grain splits is necessary according to most of the collaborators' remarks, while one of them claims it bleaches the test. One of the analysts thinks that four washings of the tanned skin are unnecessary, one washing being sufficient, while the others claim that the skins need a thorough washing and one regards it as an essential feature.

Mr. Armstrong suggests that the following changes be made in his method.

In using pickled skivers they should be made alkaline by soaking in a saturated lime water solution (if they have not been pickled with H_2SO_4) before applying the ammonium chloride solution. It has been found out that ammonium chloride will not remove sodium hydroxide from the skins. The skins should be soaked four hours in the first alcohol bath, over night in the second. They should be placed two hours in first ether bath, over night in the second. The skins if dried may be soaked up in alcohol instead of ether, if desired. Tannage should take place in a three per cent. solution and 125° F. is not too high in temperature and it evaporates the ether more completely. If the skins are resoaked in alcohol, cooler liquors may be used as the water removes the alcohol by solution. After tannage is completed wash 4 times in water at 35° C., squeezing out each time. Otherwise the method should be followed as outlined.

Recommendations.

1. That the "Armstrong Method" shall be given further investigation.

2. That the following method which apparently gave the best results be tried further by a larger number of collaborators.

Method for Color Testing.

Skins for "Color Testing" should be preserved in boro-phenol solution (one per cent. carbolic acid, two per cent. boric acid) which should be kept acid to blue litmus paper at all times, by changing the boro-phenol whenever the skins may have neutralized the acid.

Preliminary Washing.

Place the skins cut to the desired size in distilled water (20-25° C) for 24 hours, changing the water and squeezing the skins frequently in order to remove all traces of "boro-phenol" solution.

Tannage for Sheep Skin.

Lay away the washed skins in a sufficient amount (200 cc. for tests two inches by three inches in size) of three per cent. tannin solution (20° to 25° C.) for 16 hours.

Tannage for Cow Grain Splits.

Lay away the washed skins in a sufficient amount of one per cent. tannin solution for three hours, after which,

Lay away in a sufficient amount of two per cent. tannin solution for three hours, then,

Lay away in a sufficient amount of three per cent. tannin solution for 24 hours.

After Treatment for Sheepskin and Cow Grain Splits.

Wash tanned skins in four changes of distilled water 35° C. with repeated squeezings to remove excess of tan liquor, soaking ten minutes between each change. Slick lightly, tack on board, oil cow grain splits, but not sheep skins, with pure cod liver oil. Place in cool, dark, well ventilated place to dry.

The chairman wishes to thank the collaborators in this work, and hopes that it may be of benefit to the association.

DISINFECTION OF IMPORTED HIDES.*

By John H. Yocum.

(Address before National Association of Tanners, Chicago, Oct. 31st.)

At the last annual meeting of the American Leather Chemists' Association, a discussion arose as to the proper methods of disinfection and fumigation of hides, and it was suggested that the writer investigate the various methods so far suggested, and present a report to the association.

It must be admitted that the association should investigate the various methods of disinfection, in that a method adopted by the Government should have the sanction of the leather trade, as well as being as near as possible a perfect method of destroying germs. It is not only of interest to the leather trade, but such methods as are adopted by the government will affect wool, bones, hoofs and hair, all of which are capable of carrying anthrax, foot-and-mouth disease, and other diseases of cattle and sheep, as well as of man.

The methods as outlined by our government are for one reason or another inefficient or destructive of hide substance. In answer to a letter written to the Department of Agriculture, Bureau of Animal Industry, I have received the following as to the present methods of disinfection:

"Concerning new regulations governing the disinfection of hides intended for shipment to the United States, you are advised that under date of June 4, 1913, on recommendation of this department, the Treasury Department issued the following order:

"To officers of the customs and others concerned:

"Your attention is invited to that section of the regulations governing the disinfection of hides contained in T. D. 30,583 (Circular 23) of May 2, 1910, which sets forth the three methods of disinfection that will be permitted, except in the case of hides shipped from a district where anthrax is prevalent, under the supervision of a representative of the consul. (These methods being:

"1. By immersion in a 1 to 1,000 solution of bichloride of mercury.

* *Shoe and Leather Reporter*, Nov. 6, 1913.

"2. By immersion in a 5 per cent. solution of carbolic acid.

"3. By exposure to the fumes of sulphur dioxide in a room tightly closed—hides suspended separately—at least four pounds of sulphur burned per thousand cubic feet of air space—hides to be subject to the fumes at least six hours.)

"In accordance with the recommendation of the Secretary of Agriculture, the second of these methods of disinfection is hereby amended so as to read as follows:

"2. By immersion in a 5 per cent. solution of carbolic acid, or in lieu of the immersion of the hides and skins in the disinfecting solution green or wet salted hides and skins may be packed in water-tight casks, and the bundles or bales of hard, dried hides and skins may be wrapped in suitably strong and tightly woven bagging, which bagging must immediately prior to such use be thoroughly soaked in a one to one thousand bichloride of mercury solution, or in a 5 per cent. solution of carbolic acid.

"The Secretary of Agriculture also informs the department that shipments of clean hollow horns, dried and seasoned, from which have been removed the horn piths, pieces of hides and tendons, and all such portions as could be considered as glue stock, do not require disinfection, but that if shipments contain horn piths and pieces of hides and tendons, they should be classed as glue stock and be subject to the disinfection required in the regulations for glue stock. The Secretary of Agriculture expresses the further opinion that bones would likewise have to be clean and free from such other animal by-products in order to be free from the requirements for disinfection.

"The Secretary of State has been requested to instruct consular officers accordingly."

The propositions outlined by the government do not meet the requirements of proper disinfection, which at the same time would be satisfactory from the tanner's point of view. As outlined in the report made to the A. L. C. A. in November 1910, immersion in a 1 to 1,000 solution of bichloride of mercury cannot possibly be effective. By immersion in a 5 per cent. solution of carbolic acid (a saturated solution of carbolic acid), disinfection will not be effective and destruction of hide substance will

occur. By exposure to the fumes of sulphur dioxide in a room, no proper disinfection of hides will result, and destruction of hide substance will occur. I can only, in this respect, give a portion of the report read in November 1910, as follows:

"Mr. Beye, in a letter sent to the members of The National Association of Tanners, May 16, 1910, states—'This office has reason to believe that any system of disinfection now existent is absolutely without effect with respect to anthrax, and that therefore all measures adopted by the government, the primary purpose of which is to kill the anthrax germ, are unnecessary burdens to the tanning industry.'

"It appears that this is literally true, but by a modification of the first method the destruction of anthrax as well as all other germs and spores can be effected without injury to the hides or skins so treated.

"The trouble with the 5 per cent. solution of carbolic acid is that it is difficultly soluble in water and will not act on fats, and in the presence of fats has no antiseptic properties, and being acid in its character and having tendencies to injure animal matter, a solution of this strength will cause burned spots in the hides, as well as in the case of green salted hides, draw the salt on pickle from the hide, which leaves it in an uncured condition, and even then does not produce a satisfactory destruction of the anthrax spore.

"Exposure to the fumes of sulphur dioxide or burned sulphur as under Rule 3, is not only inefficient as a disinfectant, but may occasion all sorts of trouble to the hides, and is not feasible on account of the apparatus necessary for its use.

"In the case of Rule 1, like most of the salts of mercury, sublimate forms insoluble compounds with albuminoids, (as the albumin of the blood) and has then no longer any effect on bacteria. This reaction is prevented by the addition of five parts of salt per 1,000 of solution. Salt forms with mercuric chloride a double salt soluble in water, even though the water be hard and contains lime and magnesia in solution.

"Dr. R. Koch who made very exhaustive researches on the efficiency of various antiseptics, used the anthrax spore as a control test for the strength of antiseptics. He found that this

spore was the most difficult of all to kill, and the custom among bacteriologists since has been to use this spore for the purpose of determining the strength of germicides, as well as the relative measure of germ resistance.

"Comparing phenol (carbolic acid) with mercuric bichloride, he states that in a 1 per cent. solution of phenol, the anthrax spore was not killed in 24 hours, but in a 5 per cent. solution it was killed in 20 hours. The anthrax bacillus was killed by a 1 per cent. solution of phenol in one hour. Phenol has no antiseptic properties when acting on fats.

"Mercuric bichloride in a 1 to 24,000 solution kills the anthrax spores in 20 hours. The anthrax spore was killed in a 1 to 1,000 solution in 15 minutes, and germination of the spore was prevented in solutions of 1 to 70,000.

"Evans found that the anthrax spore was killed in a 1 to 1,000 solution of bichloride in 15 minutes. The bacilli themselves were killed in one minute by a 1 to 15,000 solution.

"Koch, White, Evans and Wilcox all agree on the fact that mercuric bichloride destroys the bacillus and its spore in a very short time in a 1 to 1,000 solution, provided the action of the albuminoids in precipitating the mercuric bichloride be prevented."

According to the recommendations of the United States Government and the action of the Secretary of State instructing consular agents to act accordingly, treatment of the bagging over hides in bales or bundles seems to be sufficient, for the recommendation as amended reads "or in lieu of the immersion of the hides and skins in the disinfecting solution green or wet salted hides and skins may be packed in water-tight casks, and the bundles or bales of hard, dried hides and skins may be wrapped in suitably strong and tightly woven bagging, which bagging must immediately prior to such use be thoroughly soaked in a one to one thousand bichloride of mercury solution, or in a 5 per cent. solution of carbolic acid."

This measure seems to be wholly related to infections brought about by contact with bales, but in no manner would prevent anthrax, foot-and-mouth disease, or other infective diseases

which spread through contact or association with the content of the package or cask, and therefore while occasioning an equal cost to the exporter, is not effective, in that when these bundles, bales or casks are opened at the point of receipt, any infection may be carried to human beings, as well as cattle and other animals, it being no protection to the hide sorter in Boston or New York, or to the hide worker at the tannery, from which this hide or pelt is changed into leather, or is pulled, if it so happens that it is wool skin. In respect of this the regulation is weak, and is only apparently the result of the action of the English officials in compelling the steamship companies to protect other parts of their cargo from infection during shipment.

Mr. Alfred Seymour-Jones has gone before the Board of Agriculture and Fisheries of Great Britain, and presented to them a method for disinfection of hides, which consists in a treatment with formic acid and bichloride of mercury in the presence of salt. The report made by a departmental committee in Great Britain states that any import which may have formed part of an infected animal or been exposed to infection, and other goods which may have been in contact with them, must be considered dangerous if such articles are subsequently brought into contact with suspectible animals.

Those articles open to suspicion are hay and straw, milk and milk products, hides and skins, heads and feet, carcases in skins, vaccine seed lymph, hoofs, horns, bones and other animal offals, and persons and their clothing. In the North American Continent there is no probability of importation of hay and straw, or milk and milk products, except where straw is used for packing imported articles, the straw having been exposed to infection before used as packing. Persons and their clothing are not as liable to carry infection into this country as they are into England from the Continent, because of the length of time necessary for transportation of the individual being sufficient to develop the germs and permit of the proper diagnosis of the case. It remains then that hides and skins, hoofs, horns, bones and glue stock, as well as wool and fur, are the main sources of infection.

The report of the committee appointed by the President of the Board of Agriculture and Fisheries to inquire into the foot-

and-mouth disease, presented to parliament in 1912, reads in part as follows:

"Means by which the virus of disease may be imported.

"Any imports, such as hides, etc., which may have formed part of an infected animal or been exposed to infection, and other goods (such as grain, food-stuffs, etc.) which may have been in contact with them, must be considered dangerous if such articles are subsequently brought into contact with susceptible animals in this country.

"The committee recognize that it is impracticable, even if it is not impossible, to erect an impregnable barrier against the introduction of disease, but it is agreed that the risk is greater with certain articles; those most open to suspicion being—

"(a) Hay and straw.

"(b) Milk and milk products.

"(c) Hides and skins, heads and feet, carcasses of calves in skins, vaccine seed lymph.

"(d) Hoofs, horns, bones and other animal offals.

"(e) Persons and their clothing.

"(a) The importation, from certain scheduled countries, of hay and straw for use as fodder was prohibited by the Foreign Hay and Stray Order of 1908. By and amending order of 1912 this importation is now prohibited except from such countries as are scheduled as being free from disease.—Respecting hay and straw used for packing, it appears that over 60 different imported articles are so packed, and it cannot be disputed that a large proportion of this packing ultimately reaches the farm as manure.

"The committee have given the subject their careful consideration, and the only conclusion they can arrive at is that this packing constitutes a source of danger. In view, however, of the serious dislocation of general trade which it would entail, they are not prepared, until there is further evidence against it, to advise its prohibition.

"The committee, therefore, recommend that agriculturists and persons using such hay and straw should be warned by the Board of Agriculture and Fisheries through Chambers of Agriculture and Commerce, and local authorities, and in any other way the

Board may think advisable, of the element of danger it contains, and of the risk of allowing it to come in contact with any animals, and that where possible it should be burned. . . .

"(c) Hides and Skins: The committee endorse the opinions of many witnesses, that hides and skins, with or without wool or fur, from an infected country, must be a considerable danger, not that they are likely to be placed in contact with a susceptible animal, but that in transit foodstuffs, carried in or on the same ships, quays, lighters, railway, wagons, carts, etc., may become contaminated, either by contact with them, or by being subsequently carried by the same agency, or through the clothes of stevedores discharging ships, or by porters handling these goods. . . .

"The committee have considered this subject with respect to the danger of importing anthrax as well as foot-and-mouth disease, and are of opinion that to require the disinfection before shipment of all such articles as hides, skins, bone, etc., which are most likely to be contaminated with disease, would be its natural solution. It is generally conceded that a disinfectant that will destroy the spores of anthrax would certainly destroy the virus of foot-and-mouth disease.

"With regard to hides and skins: These may roughly be divided into—

"(1) Wet hides and skins.

"(2) Dry hides and skins.

"(1) It was given in evidence that there was less danger from the importation of wet salted hides and skins, with regard to anthrax, than from dry hides and skins; but it seems impossible that any practical proposition with regard to their earlier sterilization could be effectually imposed by law.

"The committee would, however, call attention to the fact that if the practice of washing the insides of hides and skins, when flayed from the animal, with a solution of ½ per cent. of formic acid, or salt and cold water, before salting, were adopted, the germs of foot-and-mouth disease would be destroyed, and they trust that this method of diminishing the risk of infection may be made effective by international co-operation, and be generally acted upon by foreign exporters.

"(2) With reference to dry hides and skins: The committee have been informed of a process (consisting of their immersion for 24 to 48 hours in a solution of formic acid mixed with mercuric chloride, with a subsequent salting), which is recommended as one that will effectually destroy anthrax spores and will not injuriously affect the hides. The process has been favorably reported on by an eminent bacteriologist, and by experts in the tanning industry, who describe it as the most satisfactory method of sterilizing hides of which they have experience. It has been stated that if it were possible to sterilize all anthrax contaminated imports before shipment, outbreaks of that disease would be greatly lessened in this country, and the committee consider that the trades concerned might reasonably be asked to co-operate in order to effect such a reform.

"(d) Hoofs, horns, bones, and other animal offals: The committee are of opinion that there is a danger of introducing anthrax when these articles are imported from infected countries, and recommended that they should, as far as possible, be subjected to effectual sterilization before being used in this country.

"The committee recognize the great interests concerned in our shipping, which carries 70 per cent. of the world's sea-borne traffic, and by which undressed hides and skins to the value of about 13,000,000 Sterling were imported in 1910 for our tanning industries, and realize the fact that this country cannot move alone in this matter, as by so doing our trade might be handicapped unduly.

"The committee consider that other importing countries cannot fail to be interested in this subject, and that they would assist in determining what is the most effective sterilizing agent for this purpose, and that when this has been agreed on, they would co-operate with this country in adopting its use.

"The committee suggest that on this subject Great Britain might take the initiative and arrange for a practical experiment to take place at selected ports. If this proved a success, in that the cost was not prohibitive the hides or skins were not damaged, and the sterilization was effective, good grounds would be established for suggesting uniform international action. In any such action ample notice should be given to enable persons con-

cerned in the trade to adapt their arrangements to the new requirements.

"The Board of Trade are also concerned in this question, and the committee think that that department might be asked to—

"(1) Arrange international conferences.

"(2) Approach the United Trade Federation in the various European and American countries representing the affected trades.

"(3) Approach the various international chambers of commerce and agricultural societies.

"(4) Advise and assist the Foreign Office in its pourparlers with the Foreign Governments to arrive at a common line of action.

"(5) Instruct the exporters in the British dependencies and treaty ports in the approved method of disinfection.

"Moreover, the committee think that all shipments of hides and skins should then be accompanied by a sworn certificate as to their effective disinfection which should be attached to the bill of lading after being signed by the consul. Pending the adoption of some such process of sterilization as that described above, the carriage on board ship of hides and skins on the top of a general cargo should be prohibited.

"The committee have been informed that an international veterinary congress is to be held in Great Britain in 1914, and they urge that the subject of foot-and-mouth disease should there receive serious consideration, especially with a view to the governments of infected European countries taking joint action to endeavor to stamp out the disease on the continent.

"It is hoped that the information which will be obtained through the scientific inquiry about to take place in India will then be available and form a valuable addition to the stock of knowledge for the discussion of this disease which is creating great havoc among the flocks and herds of the world.

"The process referred to by the committee appointed by the President of the Board of Agriculture and Fisheries for Great Britain, and which is recommended as effectually destroying anthrax spores, is the process devised by Mr. Seymour-Jones, which has been accepted as being both efficient and practicable,

in that according to this method, with a price of 10 cents per pound for formic acid (90 per cent. and 62 cents per pound for mercuric chloride, the cost works out at 7½ cents per hide. The method as suggested by Mr. Seymour-Jones is as follows:

"A pit of suitable dimensions is required for the immersion of the hides. Into the pit run sufficient cold water to cover the hides contained in the pit.

"The volume of water must be a known amount.

"To this volume of water add one per cent. of formic acid of 90 per cent. strength, then after plunging to mix the acid and water, add one part mercuric chloride to every 5,000 parts of water. The mercuric chloride should be previously dissolved by heating in water. Finally plunge the whole pit well before adding the hides.

"In this pit the hides are left for 24 hours, when it will be observed that their condition is somewhat similar to that of a raw hide, only firmer. This pit completes the act of sterilization. From the sterilization pit the hides should be drawn and allowed to drain in such a manner as will permit the liquor to flow back into the pit for further use.

"After draining, the hides are transferred to a pit containing a saturated solution of common salt and water. In this case it is advisable to have a good layer of undissolved salt lying on bottom of pit before immersing hides. In this pit the hides need not be left more than one hour, when they should be hauled up and placed on a drainer, in order that the salt liquor may return to the salt pit for further use. Or if it is found more convenient, the hides may be opened out, flesh up, and hand salted, then placed in a pile for a few days before baling; or they may be again dried.

"After draining the sorting or classing, weighing and bundling may be proceeded with prior to export."

"The method that the writer devised for the disinfection of green salted hides, during the foot-and-mouth epidemic of 1908, was the use of a saturated salt solution containing one to 1,000 of mercuric chloride. The advantage of this suggested process claimed for the Seymour-Jones method is that the skins being colloidal albuminous substances, a plumping action is effected by the presence of the formic acid; this swelling of the hide being

in effect the addition of water thereto, this water containing mercuric chloride, and thereby a more complete penetration and consequently a more complete killing of germs is effected, because "the usual place of secretion of anthrax spores is on the surface of and immediately inside of a colloidal albuminous mass, such as blood clot, and the outer skin of the spore consists of similar albuminous matter. The difficulty up to the present has been to obtain a disinfecting solution which would penetrate firstly the dried blood clot, and secondly the hard skin (cell wall) of the spore. The treatment with acid solution provides a way out of this difficulty, for it causes the clot and the spore to swell, and become very soft and tender."

The efficient destruction of anthrax or any other germ by this process has been tested out from the statements of Professor Procter of Leeds and Dr. Ponder, etc., and consequently it cannot be denied that this method is absolutely destructive of the germs of anthrax in hides, bones, glue, stock, wool, hair, etc. It must be admitted, however, that by this method the cellular fats are not reached, but it is also a fact that the cellular fats are surrounded by tissue, which due to this treatment, is immune from spores of even anthrax, effectually seals the fat globules, prevents dissemination and therefore reaches every requirement for proper disinfection.

From the standpoint of sterilization of hides, immunity means that all other pathological germs have been destroyed, provided anthrax has been destroyed. Infections in this country have occurred both at receiving points such as New York and Boston, and at tanneries where the hides are worked, due to anthrax on imported hides. It is also true that certain parts of the United States seem to be breeding points of anthrax, such as the delta of the Mississippi in southern Louisana, but foot-and-mouth disease is sporadic and not indigenous to the United States, and undoubtedly the outbreaks of this are due to infections from foreign sources. Therefore there is a great necessity for proper disinfection of any material, probable to be brought into this country, which may carry infective diseases of cattle, sheep, hogs or man.

I understand that Siberian butter is being offered for sale in

the New York market, and in that Siberia is the home of anthrax, it may be that infections will enter this country through this means, although so far as the association is concerned directly, its object is to prevent infections brought in by the materials used in this trade.

On wet salted hides, because of the fact that the albuminous masses are not entirely dried out, and because of the slight aseptic action of the salt, and also because of the fact that on wet hides opportunity for dissemination of dust does not exist, little danger from even infected areas exists in the importation of wet salted hides.

Importation of dry hides, however, is constantly fraught with danger of infection from many diseases, in that the spore is of such character as to live under almost any condition, and is so minute as to be carried on a grain of dust.

The treatment with mercuric chloride and salt as stated by the writer in 1908, is eminently satisfactory on green salted hides, but because of the fact that a considerable length of time is necessary to permit of the penetration of the saturated salt, one to 1,000 mercuric chloride solution, into the dry hide, it is impractical for use on dry hides. The process outlined by Dr. Alfred Seymour-Jones overcomes the difficulty as related to dry hides, and would, if carried on with glue stock, wool, hair, and likely with bones, prevent the introduction of these diseases into the United States, if such a method was adopted by our government; the only question arising in this connection being whether the formic acid-mercury solution will subsequently permit of the sweating operation frequently pursued on dry hides here.

To determine this matter I have had two dry hides treated by the Seymour-Jones process at Pratt Institute. These were two hides obtained from Howes Bros. of Boston, of a shipment of B A's, (dry flints).

They were subjected to the following treatment:

They were soaked for 24 hours in a solution of formic acid (one per cent.), and one part of mercuric chloride to 5,000 parts of the water was added. After this the hides were drained for one hour and soaked for one hour in a saturated salt solution, that is a solution of water containing as much salt as it will dissolve.

They were then drained over night and placed in a bundle. The stock as it came from the formic acid solution had the appearance of green salted stock. The hides were fairly soft, and would pass anywhere for salted stock.

These hides were then shipped to the Hickory Tanning Co., West Hickory, Pa., where they were subjected to the customary milling and washing treatment, and sweated, the result being that there appeared to be no interference with the sweating operation due to the germicide, mercuric chloride or to the formic acid, the hides working satisfactorily through the sweat pits.

It is claimed by Dr. Seymour-Jones that his process enables the tanner to obtain one pound per hide additional weight in the finished product if his treatment is pursued, owing to the saving of soluble hide substance which is lost if the ordinary soaking, and stocking or fulling process is followed.

It must be admitted that if this process is pursued at points of shipment, instead of receiving dry hides, the probabilities are that a large number of the hides now received as dries would then be received as wet salts, in that after the operation at shipping points, few of the shippers would desire to dry the hides out again; the probabilities being that they would prefer to pay the extra freight on wet salted hides to our markets, rather than to send the hides as flint dries.

By pursuing this method, however, on hides, skins, wool, etc., absolute freedom from anthrax would be obtained in the United States, and while the cost of seven cents per hide for the operation, plus the probable additional freights, would make a noticeable expense, at the same time the ability to select hides thus treated, and the prevention of purchases of mud plastered or sun burns, would undoubtedly more than equalize this in cost in leather.

I therefore suggest that the association appoint a committee with power to confer with the government, as represented by the Bureau of Animal Industry and State Department, as well as to confer with trade organizations representing the glue and woolen industry, which would be affected by these proposed disinfection rules, and that this committee suggest to the United States government through its proper department, that our gov-

ernment confer with the British, German, French and Italian governments in respect of this whole matter.

Aside from the loss of human life, an epidemic disease of cattle, sheep or hogs, with our present shortage of supply, would be a disaster to this country, and I must bring to your attention forcibly the need of proper disinfection of imported materials. in that the well-being of the trade in general is involved. Action by our government should be of such a character as will prevent epidemics here, by proper disinfection, which at the same time will not impair the quality of the raw stock imported.

NOTES ON TANNIN DETERMINATION.

By L. Balderston.

In the laboratory of the Elk Tanning Co. at Ridgway, Pa., a large number of liquors and extracts are handled, and the many devices which have been worked out in the interest of convenience and speed may possibly be of interest to some other chemists. I shall therefore describe in these notes some of our ways of doing things, without claiming credit for anything which the reader may think good, as our methods are the result of the combined ingenuity of many men.

We have found that in taking the barkometer of liquors it is necessary in many cases after shaking up the bottle and pouring the liquor into the copper cylinder to wait some time, often two or more minutes, for the air-bubbles to rise, before a correct reading can be taken. We therefore use a long sink, in which we stand a row of 16 cylinders, letting the bubbles settle out of one half while the other half are being read. For liquors from 12 to 95 degrees barkometer, we use dilutions ranging from one-fifth to one-fortieth. These dilutions are made for the most part by means of special pipettes. The scheme is outlined in the table which follows.

Some error is involved in assuming that 200 cc. of a liquor from 12 to 14 degrees are equivalent to 200 grams, and for the higher dilutions we make this error negligibly small by using a pipette which holds almost the exact number of grams of liquor

TABLE OF DILUTIONS.

Barkometer range		Dilution	Mark on pipette	Capacity of pipette, cc.	Dilute to
Up to 9°	....	$^1/_3$	..	..	900
10–11° inclusive	....	$^1/_4$	200	200.0	800
12–15° "	....	$^1/_5$	200	200.0	1,000
15–17° "	....	$^1/_7$	$^1/_7$	140.6	1,000
18–21° "	....	$^1/_8$	$1/8$	122.6	1,000
22–27° "	....	$^1/_{10}$	$^1/_{10}$	97.6	1,000
28–32° "	....	$^1/_{12}$	$^1/_{12}$	80.9	1,000
33–40° "	....	$^1/_{15}$	$^1/_{15}$	64.3	1,000
41–56° "	....	$^1/_{20}$	$^1/_{20}$	47.7	1,000
57–67° "	....	$^1/_{25}$	$^1/_{25}$	37.7	1,000
68–80° "	....	$^1/_{30}$	$^1/_{30}$	31.0	1,000
81–95° "	....	$^1/_{40}$	$^1/_{40}$	23.0	1,000

necessary to make the dilution correctly. We have found that for our work it is most satisfactory to aim at 0.6 gram total solids in the analysis solutions of liquors, instead of 0.7 as prescribed in the official method. Suppose then it is desired to figure out the dilution for a liquor of 25 degrees. Assuming that each degree barkometer corresponds to 0.24 per cent. total solids, a 25 degree liquor would have 6 per cent. solids. To reduce it to 0.6 per cent., or 0.6 gram per 100 cc., it must be diluted to one-tenth its present strength. This may be done by diluting 100 grams of the liquor to one liter. One hundred grams of a 25 degree liquor will be 100 divided by 1.025 cubic centimeters, or 97.6 cc., nearly. For liquors from 22 to 27 degrees, 97.6 cc. are nearly enough equal to 100 grams to serve our purpose. For the 22 degree, the exact amount would be a little more than 97.8 cc. The error thus introduced amounts to only about one-fourth of one per cent. in the divisor, and for an average liquor this would make less than 0.01 per cent. in the result. In pipetting the 100 cc. of solution for evaporation, it is universal to neglect its excess over 100 grams, but if we were to use 100 cc. of a 25 degree liquor and dilute to 1,000, the divisor would be nearly 2.5 per cent. too small, and if the liquor really had 3 per cent. tannin, our result would be about 3.07 per cent.

The cylinders in which we make the dilutions have but one mark, at 1,000 cc., and are fitted with No. 6 rubber stoppers. They were made to order, and cost less than the regular graduated cylinders. They are less liable to breakage than the latter

because they have no ground stoppers. We have some graduated ones which we use for the occasional liquors which fall below the strength for one-fifth dilution. Thus a 7 degree liquor would be diluted by measuring out 300 cc. and making up to 900, and a ten degree by diluting 200 cc. to 800.

In general, except at the beginning of the week, the first job on the liquors in the morning is to fill up the cylinders with water not colder than about 65 degrees F., the barkometer readings having been taken the afternoon before, and the proper amount of liquor pipetted into each cylinder. From each cylinder, after filling and shaking up, 100 cc. are pipetted for total solids, and these dishes are put on trays and set away. To receive the soluble solids filtrate and the non-tannins, we use rather heavy plain tapering tumblers, which may be handled rapidly and carried in stacks of 12 with small danger of breakage. They are of clear, colorless glass, so that a fair decision may be made on the clearness of a filtrate.

For non-tannin determinations, we use a uniform charge of 30 grams of wet hide, squeezed to as nearly as possible 73 per cent. of water. The shaker jar thus contains 200 plus 73 per cent. of 30 grams, or 222 cc. of water, very nearly. In pipetting the non-tannins, we use a pipette holding 111 cc., and so marked. This amount being equivalent to 100 cc. of the original solution, some figuring is saved on the non-tans. All our liquor pipettes have large openings for the sake of rapidity in filling and emptying.

In placing the dishes on the oven, we put the total solids, soluble solids and non-tans from each liquor together. The three are entered on one page of the note-book, and in the afternoon the weights of the dishes are written in, so as to save time in the weighing. All the weighings for each liquor are thus entered one after another on the same page. The multiplication by the dilution figure, and all other figuring are done afterward by the office force, right on the page where the weighings are entered. Thus mistakes can often be traced and corrected without having to repeat the analysis.

For weighing out extracts, we use 50 cc. beakers, numbered and weighed. These are kept on a rack consisting of pegs stuck in a square piece of pine plank, easily carried about. Each

beaker has its own peg, and if one is broken, an empty peg gives warning not to use a wrong weight. For liquid extracts, the practice of our most expert man is as follows: Place the beaker on the left pan, and on the right the sum of the weights of the beaker and of the desired amount of extract. Turn the milled head of the beam-arrest a little, so as to allow the pointer to swing a few divisions to the left. Pour extract into the beaker, as it sits on the balance, in a steady stream, until the pointer swings to zero. With our balances, this happens (under the push of the pan-arrest) when the amount of extract is about 1 gram short. Then push in the pan-arrest, and thin the flow to drops. At about eight drops after the first swing of the pointer, in the case of a liquid chestnut extract, it will swing again. Then stop pouring and finish the weighing. I prefer to put on weights about 0.1 gram short, and after the first swing of the balance push in the pan-arrest and set it, holding a spatula in my right hand with which to cut off the stream at the second swing. Either of these methods is capable of giving weighings well within 0.1 gram of the amount aimed at, every time. It is easy to make a weighing in two minutes, and our expert does 24 in half an hour without hurrying. It is hard to see how a method involving the use of covers could be better than this, as that would necessarily take more time.

Our apparatus for washing in the extracts is a considerable improvement over the wash bottle. We have a tin-coated copper tank with a hinged lid, holding about 25 liters, supported on iron brackets against the wall, with a ring gas-burner under it. It is about 2 feet above the work-table, so the water will flow with some force through a glass jet, connected through a one-fourth inch rubber tube to a cock at the bottom of the tank. The flasks are set in a row on the table, and when the water has reached 85° C., the first 50 cc. beaker is laid on its side in a 4-inch funnel sitting in the neck of the first flask in the row. A stream of water from the glass jet quickly washes the extract into the flask, and neither fingers nor tongue are scalded. The funnel is moved to the next flask, and the jet thrust down into the neck of the funnel, the water being allowed to flow while from a three-eighth inch tube connected to another cock on the

tank, a rapid stream fills the first flask to the 900 cc. mark. The second sample is now washed in, into 200 or 300 cc. of hot water which have run in from the jet. The whole process for 24 samples takes about 40 minutes, including shaking.

While the filters for the soluble solids are being prepared, we catch the liquor in small lipped tumblers. When ready to collect filtrate, we replace the tumblers with bottles of about 150 cc. capacity, into whose necks the stems of the funnels fit pretty closely. These bottles have a ring etched around them with diamond ink at the 100 cc. level, for obvious reasons.

The non-tans are pipetted with 117 cc. pipettes, based on a charge of 46 grams of wet hide at 73 per cent. water. Needless to say, we do not use pipettes with large openings in extract work. In order to control the moisture in the hide-powder, it is weighed carefully air-dry, and the weight of the wet cloth being known pretty closely, the hide is squeezed to the right weight to give 73 per cent. water.

We save a good deal in breakage of dishes used in exaporating and drying by our method of handling and washing. As fast as they are weighed the dishes are placed in wooden skeleton racks holding 30. When a rack is full, a skeleton lid is put on, and the rack plunged into a tank of hot 1 per cent. borax solution large enough to hold three racks. The borax solution does not appreciably reduce the weight of the dishes if the temperature is not allowed to get above 80° C., and it soaks the dried film off much more quickly than plain water. After soaking about 15 minutes, the tray is withdrawn and put into a box between two sets of water pipes having one-thirty-second-inch holes after the manner of a needle bath. Our town water supply furnishes 90 pounds per square inch pressure, so the needle bath rinses the dishes pretty thoroughly. They are then taken out, any spots which remain being washed off by hand, and hung on pegs to dry.

We have for some time used dishes having fire-polished edges, and find that they suffer much less from loss of weight due to chipping of the edges than those with ground edges which we formerly used.

ABSTRACTS.

By-Products of the Extract Industry. G. A. KERR. *S. & L. Rep.*, Sept. 18, 1913. Spent chestnut wood, as at present used, has little fuel value. In order that the chips may be available for paper pulp they must be free from bark, black knots, decay, etc. The wood must therefore be sorted, and that intended for pulp barked and cleaned, and leached in a separate leach house. Bass wood and some others yield more pulp than chestnut chips, and are more easily digested and bleached. Destructive distillation of the chips yields acetic acid and wood alcohol, so this method of utilizing them has been suggested, but no demonstration on a commercial scale has been made. The most promising outlet for spent wood is in the direction of developing its full fuel value. Acids are developed in large quantities during the process of extract manufacture, and these may be recovered by passing the vapors from the first two or three effects through milk of lime, which combines with the acetic acid to form soluble calcium acetate. This process not only furnishes a salable product, but lengthens the life of the extract plant by removing the corrosive acids from the vapors, thus preventing the corrosion of copper pipes and pans. Another by-product, which is beginning to be made in Europe, is an extract for drumming or dry dipping made by re-extracting the spent chips.

Stehlenert's Process for Spent Lyes from Pulp Mills. J. F. BRIGGS. *Chemical World,* Nov. 1913, pp. 346-8. The process is based on the decomposition of the soluble compound of lignin and sulphurous acid by the action of sulphuric acid at a high temperature under pressure. Oxygen is supplied in the form of compressed air, which serves also to cause the precipitated lignin to assume a granular instead of a gelatinous form. The amount of sulphuric acid used must be very small in order to avoid carbonization of the product, and it is found that the oxidation of the trace of sulphur dioxide left in the waste liquors furnishes a sufficient quantity of acid. The lime is first removed by precipitation with sodium bisulphate. The precipitated calcium sulphate is washed and so furnishes a salable product. The lime-free lye is run into an autoclave and heated to the boiling point. Air is pumped in until the pressure reaches 250 pounds per square inch. The chemical action which sets in at this stage causes a rise of 36° F. The autoclave is further heated to 320° F. At this point the free SO_2 has all been oxidized to sulphuric acid. Heating is continued, and at about 330° F. the lignin compounds begin to decompose, causing a rise of 36° F. The temperature is now forced up to about 400° F., when the reaction should be complete. The liberated SO_2 is passed into towers to make fresh liquor for the digestion of pulp. The lignin is dried by waste heat, and may either be used as fuel or treated by destructive distillation for the production of acetic acid and wood alcohol. The inventor believes that the yield of lignin may entirely replace other fuels in the wood-pulp process. The value of the recovered sulphur is almost as much as the whole cost of the treatment.

Neradol. W. MOELLER. *Collegium*, 1913, 593-7. Further objections to the opinions of other chemists in regard to the character and value of Neradol. L. B.

Neradol. E. STIASNY. *Collegium*, 1913, 597-9. Reply to Moeller's strictures. L. B.

The Action of Lactic Acid on Sulphite-Cellulose. FELIX ABRAHAM. *Collegium*, 1913, 599-603. A critical examination of the results of Stutzer (abstract this Journal, last issue, p. 481.) Stutzer finds that an addition of lactic acid to sulphite-cellulose liquors increases their content of tanning material. Abraham explains this by stating that the acid causes a swelling of the hide, and so increases its capacity to absorb tannin and other matters. Abraham also states that in the case of sulphite-cellulose liquors, the strength of the analysis solution to a great extent influences the result. For a particular extract, the following results were obtained:

Grams extract per liter in analysis solution	Per cent. tanning substance found	Per cent. non-tans found
30.0	19.1	31.0
15.0	24.3	25.8
10.1	26.5	23.6
8.3	28.4	21.7

L. B.

The Chemical Constitution of Resinous Phenolic Condensation Products. L. H. BAEKELAND. (Address.) *Jour. Ind. & Eng. Chem.*, 1913 [5], 506-11. After some mention of the new industrial applications of these substances, the speaker takes up his main theme, the theory of the subject. Resinous and amorphous substances do not invite chemical research and not much attention was given to these by Bayer and his pupils (1872 and later) or Kleeberg (1891) in their studies of the condensation products of aldehydes with phenols. The simplest reaction (Lederer, Manasse, Bayer) is the condensation of formaldehyde with phenol to saligenin (*o*-oxybenzylalcohol);

$$C_6H_5OH + CH_2(OH)_2 = C_6H_4\begin{cases} CH_2OH \\ OH \end{cases} + H_2O$$

p-oxybenzylalcohol is formed at the same time. To prepare saligenin special care in details is needed since it is easily dehydrated and resinified. The resinous dehydration products from phenol alcohols are called saliretins. Various formulae have been assigned such as $C_{14}H_{14}O_3$, $C_{28}H_{26}O_5$, $C_{56}H_{50}O_9$. These are purely conjectural and impossible to prove. It is probable they have more complicated molecules and are mixtures in colloidal solid solution. DeLaire (1905) was one of the first to patent fusible saliretin products, substitutes for shellac, copal, etc. These are condensation products of saliretin and phenol alcohols and can be made in one operation without isolation of the intermediate condensation pro-

ducts. Blumer's fusible resin (1902) and DeLaire's, practically identical, retain their fusibility on further moderate heating because they contain free phenol. The speaker has isolated *p*-dioxydiphenylmethane $HO—C_6H_4—CH_2—C_6H_4—OH$ together with the oxybenzylalcohols from the initial mass used in condensation, indicating that diphenylmethane compounds are formed in the resinification process. Dr. Raschig has pointed out that this would render possible a great many isomers in the ultimate products and identification would be hopeless. He considers the soluble resin to be a mixture of the three isomeric dioxydiphenylmethanes which however does not agree with the fact that boiling water extracts very little of these easily soluble, crystalline substances. The speaker has produced a fusible phenol resin by heating *p*-dioxydiphenylmethane with paraform under pressure; increased proportion of paraform yielded hard, infusible resins of high chemical resistance. On the other hand the fusible resin was obtained by reducing salicylic acid, indicating its salinetin nature. He designates these fusible resins under the general term of Novolak. They have not been successful in varnish manufacture.

These are related to another class of hard, infusible resins, bakelite, resinit, condensite, classed by Lebach as "resites." Being infusible, insoluble, chemically inert and originating from variable mixed phenols, it is still more difficult to assign formulae. In their manufacture, the formaldehyde may be replaced by other methylene compounds. After the condensation reaction, the molecules polymerize, giving products of increased molecular weight and high resistance. From the speaker's early experiments, he concluded that a dehydration product of six molecules saligenin and one molecule formaldehyde was a typical representation; increasing the ratio of saligenin lowered the resistance of the product. Raschig, while assuming that dioxydiphenylmethanes take part in the condensation reactions, also distinguishes the bakelite from the soluble resin substitutes as resulting from an increased proportion of formaldehyde in manufacture. The speaker emphasizes that the nature of the condensing agent is also important. Raschig states that neither *o*- or *p*-oxybenzylalcohol alone will yield bakelite but a mixture is necessary. The speaker heated both alcohols singly and mixed together with alkali in sealed tubes and obtained hard resins (polymerized saliretins) inferior to bakelite in resistance, but infusible. On heating *p*-oxybenzylalcohol with five per cent. paraform (equivalent to six molecules phenol to seven and one-fourth molecules formaldehyde), products equal to bakelite were obtained. Ammonia may be used as a contact reagent in the condensation of phenol with formaldehyde. Hexamethylenetetramine (the condensation product of formaldehyde and ammonia) yields with phenol the same hard, infusible resin. W. J. K.

Difficultly Soluble Tanstuffs. E. O. SOMMERHOFF. *Collegium*, 1913. 531-3. Commenting upon Dr. Moeller's recent paper on this subject the criticism is made that one important point is neglected, namely that in-

soluble tans to tan well should be freshly precipitated For example, quebracho solutions are boiled before use and let cool quickly to obtain freshly separated phlobaphenes. Another method of retarding the coagulation of recently precipitated colloids is the addition of a restraining colloid, for instance rice meal added to Chinese gambier. In tannin analysis by hide powder, difficultly soluble extracts (quebracho) behave towards cold water like hydrolyzable salts and since both components have tanning power, it is incorrect to sharply differentiate soluble and insoluble tans. As to the solvent action of $HNaSO_3$ on insoluble tans favoring rendement, it may be said that the addition of any crystalloidal non-tan to any colloidal suspended or dissolved absorption agent is beneficial. Examples are alkaline chlorides or sulphates added to the colloidal basic Al or Cr sulphates (which have resulted from the hydrolysis of the crystalloid salts during tannage). With aromatic colloidal tannins Na_2SO_3 and sometimes Na_2SO_4 (with neradol) are used.

W. J. K.

The Action of Dog Puer Bate. JULIUS WOHLGEMUTH. *Collegium*, 1913, 585-6. Two theories have been held: (1) the action is purely chemical, the alkalies and acids of the puer removing the lime and dross from the pelt; (2) the solution is effected by fermentation. There is no doubt that ferments play an important part here, although it has not been proven that trypsin from the pancreatic juice is the only one. Others from the gall and intestinal juices are present which may share in the effect. To distinguish the effect of each, the author proposes to compare (with the normal) three special sorts of dog dung secured from (1) a dog from which the pancreas has been removed; product trypsin free, containing only intestinal and gall ferments. (2) a dog provided with a fistula leading the gall away externally; dung containing only pancreatic and intestinal ferments. (3) a dog with gall fistula and without pancreas; dung containing only intestinal ferments.

The author announces that such experiments are in progress and reserves this field of work. W. J. K.

Physiological Remarks on Hide and Bark from the Tanner's View-Point. (Address.) B. KOHNSTEIN. *Collegium*, 1913, 587-593.

Coloration of Hide.—The most important pigments of the hide are hemosiderin containing iron, and iron free melanin. The deposition of pigments in the skin interests the tanner in the case of ornamentally marked reptile skins used for leather. Further mottled skins, containing colored pigment cells, especially black, must be sorted out to avoid uneven tones in glove leather dyeing. Still worse are the blue black discolorations developing in the hide after death. The speaker has produced these fermentation colorings during a second salting of salted calf skins. One portion was treated with pure salt, the other with salt drenched with fresh ox-blood. After eight weeks the skins treated with blood were much the warmest and on dehairing showed the blue black colora-

tion; the others remained pure white. The iron of the hemoglobin of the blood is here active. Similar local colorations are formed on contact of the hide with rusty iron. According to Unna, tyrosin is the reducing component of the horn substance which readily takes up metallic oxides. In hides rich in fat, the fat mass also precipitates metallic oxides, causing fermentation.

Dyestuffs of Tan Bark.—In the young bark chlorophyll is the main coloring substance; with increasing age the barks become brown. Researches by vârious investigators are cited; among others A. G. Perkins found a dyestuff quercetin accompanied by myricetin of complex phenol constitution; the last causes the green color of alkaline solutions. Hertzig found that quercetin in alkaline solution absorbs oxygen vigorously forming myricetin. Keegan on the other hand found that on boiling colorless aqueous solutions of various tannins with dilute HCl a soluble dyestuff was formed which gave a green color with NH_3 or $Ba(OH)_2$. The red coloring substance of autumn leaves behaves similarly. He assumes that all tannins contain a phenolic chromogen nucleus represented in such tannoids as quercetin, rutin, luteolin, gentisin, galangin; on oxidation red colors are formed.

The speaker has studied the dye stuffs of tan barks; their reactions are important in identifying the accompanying tannins. On precipitating the tans by albumoses (peptone Witte), the colorless filtrates on treatment with alkali and shaking, through oxidation give colors; dye woods act similarly. When the extracts of the barks of the Abies and Larix species are precipitated by albumoses, the filtrates give brown to deep red with alkalies. In pine liquors from the tannery, however, a green color is met with which increases in intensity according to the amount of lime retained by the pelt. This color is also found in leather when washed with alkaline soaps. The speaker finally succeeded in extracting the dye stuff from spent conifer bark which had been leached with cold water down to a tannin content of four and one-half to five per cent. With higher tan content or hot extraction, the attempt failed. The leaf green color is obtained by boiling the extract with HCl and adding NH_3 after filtration. It is concluded that enzymes are present in the bark of Abies Canadensis, Pinus and Larix which split up the dye stuffs into substances giving the green reactions. Willow bark gave a similar result. If these green solutions are shaken with air while still warm, they become red and on cooling and diluting, again green. By prolonging the heating and blowing in air, the green color no longer returns. The dyestuff in question is now being isolated for analysis. It identifies a pine tanned leather and can be detected after years of storage. Some other species of bark gave a weak fugitive reaction of the green color. W. J. K.